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METALLURGICAL CALCULATIONS

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METALLURGICAL CALCULATIONS

BY

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PART I.

Introduction, Chemical and Thermal Principles,
Problems in Combustion.

SECOND IMPRESSION OF
SECOND EDITION.
Revised and Corrected.



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PREFACE.

The larger part of the contents of this book is a reprint of a serial running in the "ELECTROCHEMICAL AND METALLURGICAL INDUSTRY" from March, 1905, to March, 1906. To these has been added the statements of a number of problems for practice, which it is hoped will still further increase the usefulness of the work. It is intended that the serial which is now appearing during 1906 shall appear as Part II, and that which shall appear during 1907 as Part III, completing the work.

To those who are practically conversant with metallurgical operations, no argument need be offered as to the value of properly made calculations concerning the running of a process. To those who are engaged in teaching, it need only be said that if the value of metallurgical problems as a means of teaching metallurgy is doubted, try the plan and see how wonderfully it succeeds. To artisans or students working alone, it may be said that the mastery of such problems and their working principles constitutes the practical mastery of metallurgy as a science, and leads inevitably to a strong and commanding grasp of the subject.

If ever rule-of-thumb is to be replaced in a metallurgical process by scientific operation, the change must be based on experiments, classification of results, and calculations therefrom. The principles involved are physical, chemical and mechanical; the scientific metallurgist must master these, use them as tools, and overcome brute nature by their skilful employment.

Every metallurgical problem is an exercise in pure logic and mathematical reasoning; the premises are observed facts—all that can be learned of the process by direct observation and measurement; the conclusions desired are everything which can be deduced from the premises by hook or by crook, by direct logical process or by inference. In this way data and

information are obtained which cannot be directly observed or measured, and which are of the most essential value for thoroughly understanding the process.

To the study of this hitherto somewhat neglected and yet amazingly fruitful side of metallurgical work the author invites the reader, and hopes that the work here presented may in itself reward everyone who spends time in reading and effort in mastering its contents.

JOSEPH W. RICHARDS.

Lehigh University,
March 12, 1906.

METALLURGICAL CALCULATIONS.

INTRODUCTION.

The making of calculations respecting the quantitative working of any process, furnace or piece of apparatus used in metallurgical operations is of the greatest importance for estimating the real efficiency of the process, for determining avenues of waste and possible lines of improvement, and for obtaining the best possible comprehension of the real principles of operation involved.

The possibility of making such calculations respecting any process, furnace or apparatus depends on skill in collecting such necessary data as can be obtained by observation or measurement, the insight or intuition to see the further use which can be made of said data when once obtained, and, finally on the possession of a working knowledge of the fundamental chemical, physical and mechanical principles involved in the calculations. The highest desideratum, all in all, however, is a plain analytical, common sense mind, capable of clear, logical thinking. It is the writer's conviction that no study of details, or even observation of plants in actual operation, can supply the insight into metallurgical processes and principles, such as is gained by these calculations, in addition to the high grade of mental training involved.

SCOPE OF THE TREATISE

Discussion of the chemical equation.

Weights and volumes of gases.

Correction of gas volumes for temperature and pressure.

Combustion of commercial fuels.

Heat of chemical combination; of combustion.

Theoretical flame temperatures:

With pure oxygen.

With ordinary air.

- With diluted air: Farley's system.
- With hot air and cold gas.
- With hot air and hot gas.
- Effect of excess air.
- Calculation of furnace efficiencies.
- Chimney draft.
- Water gas.
- Producer gas: Efficiency, effect of drying.
- Mixed gas:
 - Use of steam in producers.
 - Increased efficiency.
 - Maximum steam permissible.
- Transmission of heat through metals, brick, etc.
- Regenerative gas furnace:
 - Proportioning of gas and air regenerators.
 - Efficiency of regenerators.
 - Heat balance sheet.
 - Theoretical temperatures under different conditions.
- Gas engines:
 - Calculation of temperature in cylinder.
 - Efficiency; balance sheet.
- Cupolas: Amount of blast required.
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- Blast furnaces:
 - Balance sheet of materials.
 - Calculation of blast received.
 - Efficiency of blowing engines.
 - Power and dimensions of blowing engines.
 - Carbon consumed at tuyeres.
 - Effect of atmospheric changes.
 - Effect of the moisture in the blast.
 - Calculation of the temperature.
 - Effect of hot-blast.
 - Heat balance sheet of the furnace.
 - Power producible from the waste gases.
- Hot-blast stoves: Theory of iron-pipe and fire-brick stoves.
 - Efficiency.
- Bessemer Converters:
 - Blast required and time of operation
 - Balance sheet of materials.

- Heating efficiency of various ingredients of bath.
- Heat balance sheet.
- Theoretical rise in temperature.
- Conversion of copper matte.
- Open-hearth Furnaces:
 - Pig and ore process; calculation of charge.
 - Heat evolved or absorbed in bath reactions.
 - Efficiency of furnaces; of furnaces and producers
 - Heat balance sheet.
- Pyritic smelting.
- Electric furnaces:
 - Working temperatures.
 - Heat balance sheet.
 - Efficiency.
- Electrolytic furnaces:
 - Absorption of heat in chemical decompositions.
 - Equilibrium of temperature attained.
 - Ampere and energy efficiency.
- Electrolytic refining:
 - Calculation of plant and output.
 - Power requirements; temperature of baths.
 - Ampere and energy efficiency.
- Condensation of metallic vapors:
 - Principles involved.
 - Application to condensation of zinc and mercury.

CHAPTER I.

THE CHEMICAL EQUATION.

The calculation of the quantitative side of many metallurgical processes depends upon the correct understanding of chemical equations. Every chemical equation is capable of giving three most important sets of data concerning the process which it represents; it shows the relative weights of the reacting substances, their relative volumes, when in the gaseous state, and the surplus or deficit of energy involved in the reaction, when the heats of formation of the substances concerned are known.

ATOMIC WEIGHTS.

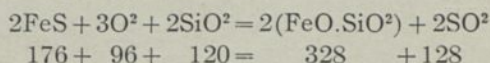
These are the basis of all quantitative chemical calculations. For metallurgical purposes we may use them in round numbers as:

Hydrogen.....H	1	Arsenic.....As	75
Lithium.....Li	7	Selenium.....Se	79
Beryllium.....Be	9	Bromine.....Br	80
Boron.....B	11	Strontium.....Sr	87
Carbon.....C	12	Zirconium.....Zr	90
Nitrogen.....N	14	Columbium.....Cb	94
Oxygen.....O	16	Molybdenum.....Mo	96
Fluorine.....F	19	Palladium.....Pd	106
Sodium.....Na	23	Silver.....Ag	108
Magnesium.....Mg	24	Cadmium.....Cd	112
Aluminium.....Al	27	Tin.....Sn	118
Silicon.....Si	28	Antimony.....Sb	120
Phosphorus.....P	31	Tellurium.....Te	126
Sulphur.....S	32	Iodine.....I	127
Chlorine.....Cl	35.5	Barium.....Ba	137
Potassium.....K	39	Tantalum.....Ta	183
Calcium.....Ca	40	Tungsten.....W	184

Titanium.....Ti	48	Iridium.....Ir	193
Vanadium.....V	51	Platinum.....Pt	195
Chromium.....Cr	52	Gold.....Au	197
Manganese.....Mn	55	Mercury.....Hg	200
Iron.....Fe	56	Thallium.....Tl	204
Nickel.....Ni	58.5	Lead.....Pb	207
Cobalt.....Co	59	Bismuth.....Bi	208
Copper.....Cu	63.6	Thorium.....Th	232
Zinc.....Zn	65	Uranium.....U	238

RELATIVE WEIGHTS.

Writing any chemical equation between elements or their compounds, the relative weights concerned in the reaction are obtained directly from using these atomic weights, which are, themselves, of course, only relative. *E.g.*, the slagging of iron in Bessemerizing copper matte:

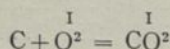


These relative weights may be called kilograms or tons, pounds, ounces or grains; whatever units of weight we may be working in. In most metallurgical work we use kilograms or pounds as the convenient weight units.

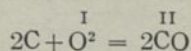
RELATIVE VOLUMES OF GASES.

Where gases are involved, the relative number of molecules of the gaseous substance concerned in the reaction stands for the relative volume of that gas concerned in the reaction. It is usual and convenient to designate these relative volumes by Roman numerals, placed above the formulæ. The following are some examples:

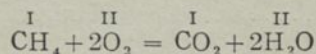
Complete combustion of carbon:



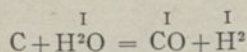
Incomplete combustion of carbon:



Combustion of marsh gas:



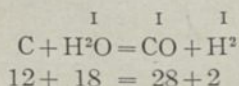
Production of water gas:



In each case above, the volume of a solid or liquid cannot be stated, but the relative volumes of all the gases taking part in a reaction are derived simply from the number of molecules of each gas concerned. These relative volumes may be called so many cubic meters or liters, or cubic feet, or whatever measure is wanted or being used. In most metallurgical calculations it is convenient to use cubic meters or cubic feet.

EXACT WEIGHTS AND EXACT VOLUMES.

If we specify or fix the weights used, as, for instance, so many kilograms of each substance as the numbers representing the relative weights, then we can, by using one constant factor, convert all the relative volumes into the real or absolute volumes corresponding to the weights used. If, for instance, we take the equation of the production of water gas:

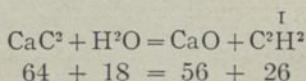


With the relative weights written beneath and the relative volumes above, then if we fix the weights as kilograms, the relative volumes can be converted into actual volumes in cubic meters by multiplying by 22.22. A cubic meter of hydrogen gas (under standard conditions) weighs 0.09 kilogram, and thence 2 kilograms will have a volume of $2 \div 0.09 = 22.22$ cubic meters. But the relative volumes show that the CO and H²O gas are the same in volume as the hydrogen, and it, therefore, follows that each Roman I stands for 22.22 cubic meters of gas, if the weights underneath are called kilograms. The consideration of these relations is very advantageous, because, by means of this factor (22.22) we pass at once from the weight of a gas to its volume; each molecule or molecular weight of a gas, in kilograms (or, briefly, each kilogram-molecule), represents 22.22 cubic meters of that gas.

The conversion from weight to volume is quite as simple using English measures; and, by a strange coincidence, the same factor can be used as in the metric system. The coin-

cidence alluded to is the fact (which the writer, as far as he can discover, was the first to notice) that there happens to be the same numerical relation between an ounce (av.) and a kilogram, as there is between a cubic foot and a cubic meter; in short, there are 35.26 ounces (av.) in a kilogram, and 35.31 cubic feet in a cubic meter. The difference is only one-seventh of one per cent., which can be ignored, and we can therefore say that if the relative weights in an equation are called ounces (av.), each molecule of gas in the equation represents 22.22 cubic feet.

Example.—The production of acetylene from calcium carbide:



Interpreting by weights, and calling the relative weights ounces, we can call the I molecule of C^2H^2 gas 22.22 cubic feet, so that, theoretically, 64 ounces of pure carbide, acting on 18 ounces of water, produce 56 ounces of lime and 26 ounces of C^2H^2 gas, the volume of which is 22.22 cubic feet.

WEIGHTS AND VOLUMES OF GASES.

The weight of one cubic meter of dry air, under standard conditions (at 0° Centigrade and at a pressure of 760 millimeters of mercury), is 1.293 kilograms. The composition of air is:

	By Weight.	By Volume.
Oxygen.....	3	21
Nitrogen.....	10	80
or, in percentages,		
Oxygen.....	23.1	20.8
Nitrogen.....	76.9	79.2

While these may not represent the absolutely accurate average composition of dry air, yet the variations are such that the above simple ratios, 3 to 10 and 21 to 80, are close enough for all practical purposes in metallurgy.

The weight of one cubic foot of dry air is 1.293 ounces (av.).

The weight of one cubic meter of hydrogen gas, at standard conditions, is 0.09 kilogram (1 cubic foot, 0.09 ounces). The formula of hydrogen gas is H^2 , is molecular weight 2; and since the densities of all gases are found experimentally to

be proportional to their molecular weights, it follows that the density of any gas referred to hydrogen is expressed numerically by one-half its molecular weight. But the weight of a cubic meter of gas is the weight of a cubic meter of hydrogen multiplied by the density of the gas referred to hydrogen; thus, is obtained the weight of a cubic meter of any gas whose formula is known. Examples follow:

Formula.	Molecular Weight.	Density Referred to Hydrogen.	Weight of 1 Cubic Meter.
Hydrogen.....H ²	2	1	0.09 kilos.
Water vapor.....H ² O	18	9	0.81 "
Nitrogen.....N ²	28	14	1.26 "
Oxygen.....O ²	32	16	1.44 "
Carbon monoxide...CO	28	14	1.26 "
Carbon dioxide....CO ²	44	22	1.98 "
Marsh gas.....CH ⁴	16	8	0.72 "
Etc., etc.			

In the case of water vapor, a particular explanation is necessary. It cannot exist under standard conditions, but condenses to liquid at 100° C. if under 760 millimeters pressure. It does exist at lower temperatures than 100°, but only under partial pressures of fractions of an atmosphere; thus, at a pressure of 1-50 atmosphere (when it forms 1-50 of a mixture of gases) it can exist uncondensed at ordinary temperatures (15° C. or 60° F.). The above weight for a cubic meter of water vapor (0.81 kilos. per cubic meter at standard conditions) is, therefore, only a hypothetical value, but it is extremely useful, because it enables us to calculate, by the principles to be explained further on, the weight of a cubic meter of water vapor under any conditions of temperature and pressure at which it is possible for it to exist.

CORRECTIONS FOR TEMPERATURE.

The volumes of all permanent gases increase uniformly for uniform increase of temperature, so that, starting with a given volume at 0° C., it is found that their volume increases 1/273 for every degree Centigrade rise in temperature. Thus, at 273° C., the volume is just double the volume at 0°. Stating this fact in another way, we may say that the gas acts as if it would have no volume at -273° C., and would increase uniformly

in volume from this point up to all measurable temperatures, the increment being, for each degree, $1/273$ of the volume which the gas has at 0° C. A still briefer statement is that the volume of a gas is proportional to its temperature above -273° C., or to its absolute temperature—the latter being its temperature in $C^{\circ} + 273$.

The converse of these principles is, that the density of a gas; that is, the weight of a unit volume, varies inversely as its absolute temperature.

In Fahrenheit degrees, we can say that a gas expands 1-490 ($1/273 \times 5/9$) for every degree rise above 32° C.; or that the volume is proportional to the absolute temperatures, *i.e.*, to the $F^{\circ} - 32 + 490$ ($= F^{\circ} + 458$).

These principles are in constant use in metallurgical calculations. Thus, one kilogram of coal will need 8 cubic meters of air to burn it, at 0° and 760 millimeters pressure. What volume will that be at 30° C. and the same pressure? Since 30° C. is $30 + 273 = 303^{\circ}$ absolute, the two temperatures will be 273 and 303, and the

$$\text{Volume at } 30^{\circ} \text{ C.} = \text{volume at } 0^{\circ} \text{ C.} \times \frac{303}{273}$$

It is always to be recommended to make such calculations in the above form; that is, to first put down the known volume, and then to multiply it by a fraction, the numerator and denominator of which are the two absolute temperatures. A moment's reflection will show which way the fraction must be written; if the new volume must be greater than the old, the value of the fraction must be greater than unity, the higher temperature must be in the numerator; if the fraction were inverted, we know that the result would be less than the starting volume instead of greater, which would be wrong.

Taking an example in Fahrenheit degrees: What is the volume under standard conditions of 175 cubic feet of gas measured at 90° F. and standard pressure (29.93 inches of mercury)? Since 32° F. is 490° absolute and 90° F. is 548° absolute, and the new volume must be *less* than the starting volume, we have

$$\text{Volume at } 32^{\circ} \text{ F.} = 175 \times \frac{490}{548} = 156.5 \text{ cubic feet.}$$

CORRECTIONS FOR PRESSURE.

The principle is that the volumes of a gas are inversely as the pressure upon it, so that doubling the pressure halves the volume, etc. Since the practical problems almost always present the pressure as two numbers, all that is necessary is to multiply the original volume by a fraction whose numerator and denominator are the two pressures concerned, and arranged with the numerator the larger or the smaller of the two numbers, according as to whether the final volume should be greater or less than the starting one. Putting the solution in this manner avoids the primary school method of making a proportion, which is so apt to be expressed upside down, and absolutely avoids error with the minimum exercise of brain power.

Examples.—What is the volume of 100 cubic meters of any gas, if the pressure is changed to 700 millimeters?

$$\text{Answer: } 100 \times \frac{760}{700} = 108.6 \text{ cubic meters.}$$

What is the volume at standard pressure of 150 cubic feet of gas measured at 28.50 inches of mercury?

$$\text{Answer: } 150 \times \frac{28.50}{29.93} = 142.8 \text{ cubic feet.}$$

CORRECTIONS FOR TEMPERATURE AND PRESSURE.

These can be both allowed for, by simply correcting first for one, and then for the other. Actually, the simplest statement is to put down the original volume, then to multiply it by one fraction, which corrects for temperature, and again by another fraction correcting for pressure, thinking out carefully for each fraction the proper way of expressing it, *i.e.*, whether it should increase or decrease the volume.

Examples.—What does 100 cubic meters of air at standard conditions become at 50° C. and 780 millimeters pressure?

$$\text{Solution: } 100 \times \frac{50 + 273}{273} \times \frac{760}{780} = 115.3 \text{ cubic meters.}$$

What is the weight of one cubic meter of hydrogen at 1000°

C. and 250 millimeters pressure, its weight at standard conditions being 0.09 kilograms?

$$\text{Solution: } 0.09 \times \frac{273}{1000 + 273} \times \frac{250}{760} = 0.00637 \text{ kilograms.}$$

What weight of oxygen is in 1500 cubic feet of dry air at 100° F. and at 28.50 inches of mercury? (Refer to weight of air at standard conditions, and percentage composition.)

$$\text{Solution: } 1.293 \times \frac{3}{13} \times \frac{490}{558} \times \frac{28.50}{29.93} \times 1500 = 374 \text{ ounces.}$$

What is the weight of 50 cubic meters of water vapor at a temperature of 30° C. and a pressure of 31.6 millimeters?

$$\text{Solution: } 0.81 \times \frac{273}{303} \times \frac{31.6}{760} \times 50 = 1.517 \text{ kilograms.}$$

$$\text{or } 50 \times \frac{273}{303} \times \frac{31.6}{760} \times 0.81 = 1.517 \text{ kilograms.}$$

The first expression calculates the weight of a cubic meter of water vapor at the assumed conditions, and multiplies by 50; the second calculates the hypothetical volume of the 50 cubic meters if reduced to standard conditions, and multiplies by the hypothetical weight of a cubic meter at those conditions.

Problems Illustrating Preceding Principles.

Problem 1.

A bituminous coal contains on analysis:

Carbon.....	73.60	Moisture.....	0.60
Hydrogen.....	5.30	Ash.....	8.05
Nitrogen.....	1.70		_____
Sulphur.....	0.75		100.00
Oxygen.....	10.00		

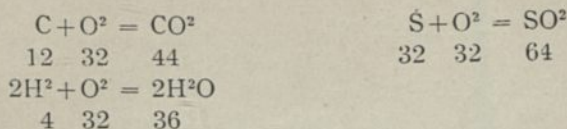
It is powdered and blown into a cement kiln by a blast of air.

Required: 1. The volume of dry air, at 80° F. and 29 inches barometric pressure theoretically required for the perfect combustion of one pound of the coal.

2. The volume of the products of combustion, using no excess

of air, at 550° F. and 29 inches barometer, and their percentage, composition.

Solution: The reactions of the combustion are:



Requirement (1):

The oxygen required for burning one pound of coal is:

Oxygen for carbon.....	= 0.7360 × 32/12 = 1.963 pounds.
Oxygen for hydrogen....	= 0.0530 × 32/4 = 0.424 "
Oxygen for sulphur	= 0.0075 × 32/32 = 0.0075 "
Total required.....	2.3945 "
Oxygen in coal.....	0.1000 "
Oxygen to be supplied.....	2.2945 "
Nitrogen accompanying.....	7.6483 "
Air necessary.....	9.9428 "
	= 159.08 ounces (av.).

Volume of air necessary (standard conditions)

$$= \frac{159.08}{1.293} = 123.03 \text{ cubic feet.}$$

Volume of air necessary at 80° F. and 29 inches barometer =

$$123.03 \times \frac{80 + 458}{490} \times \frac{29.93}{29} = 139.4 \text{ cubic feet.} \quad (1)$$

<i>Requirement (2):</i>	Pounds.
The weight of CO ² formed is.....	0.7360 + 1.963 = 2.729
The weight of H ² O formed is.....	0.0530 + 0.424 = 0.477
The weight of moisture is.....	0.006
The weight of SO ² formed is.....	0.0075 + 0.0075 = 0.015

The weight of nitrogen altogether is 7.6483 + 0.0170 = 7.6653 pounds. Converting these weights into ounces, and dividing each by the weight of a cubic foot of each gas in ounces, we have the volume of these theoretical products at standard conditions:

Volume CO ² = 2 729 × 16 ÷ 198 =	43 664 ÷ 1.98 = 22.05 cubic feet.
Volume H ² O = 0.483 × 16 ÷ 0.81 =	7 728 ÷ 0.81 = 9 54 " "
Volume SO ² = 0 015 × 16 ÷ 2.88 =	0 2400 ÷ 2.88 = 0.08 " "
Volume N ² = 7 665 × 16 ÷ 1.26 =	122.645 ÷ 1.26 = 97.34 " "
Total volume at standard conditions..... =	128.99 " "
Volume at 550° F. and 29 inches barometer =	
	$128.99 \times \frac{550 + 458}{490} \times \frac{29.93}{29} = 273.9$ " "

The percentage composition by volume follows from the above volumes as:

CO ²17.1 per cent.	N ² <u>75.4</u> per cent.
H ² O..... 7.4 "	100.00
SO ² 0.1 "	

Problem 2.

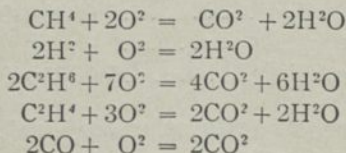
Natural gas in the Pittsburg district contains:

Marsh gas.....CH ⁴	60.70 per cent.
Hydrogen..... H ²	29.03 "
Ethane.....C ² H ⁶	7.92 "
Olefiant gas.....C ² H ⁴	0.98 "
Oxygen.....O ²	0.78 "
Carbonous oxide.....CO	0.58 "

Required:

- (1) The volume of air necessary to burn it.
- (2) The volume of the products of combustion.

Reactions:



Solution:

Oxygen required for CH ⁴ =	0.6070 × 2 = 1.2140 parts.
Oxygen required for H ² =	0.2903 × $\frac{1}{2}$ = 0.1451 "

Oxygen required for C^2H^6	$= 0.0792 \times 7/2 = 0.2772$	parts.
Oxygen required for C^2H^4	$= 0.0098 \times 3 = 0.0294$	"
Oxygen required for CO	$= 0.0058 \times \frac{1}{2} = 0.0029$	"
	<u>1.6686</u>	"
Deduct oxygen already present	<u>0.0078</u>	"
Leaves oxygen to be supplied	1.6608	"
Corresponding to air	$\frac{1.6608}{0.208} = 7.985$	" (1)

Volumes of products of combustion:

	CO^2	H^2O	N^2
From CH^4	0.6070	1.2140	
From H^2		0.2903	
From C^2H^6	0.1584	0.2376	
From C^2H^4	0.0196	0.0196	
From CO	0.0058		
From air			<u>6.3242</u>
Total products	<u>0.7908</u>	<u>1.7615</u>	6.3242 (2)

The above solution is entirely in relative volumes, which may be all considered cubic feet or cubic meters, and are true for equal conditions of temperature and pressure.

Problem 3.

A Bessemer converter contains 10 metric tons of pig iron of the following composition:

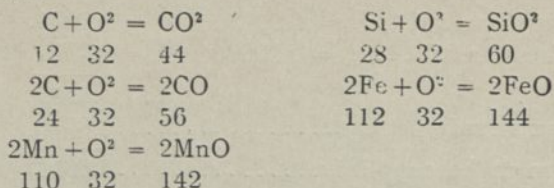
Carbon	3.00 per cent.
Manganese	0.50 "
Silicon	1.50 "
Iron	95.00 "

On being blown, one-third the carbon burns to CO^2 , the rest to CO; 5 per cent. of iron is oxidized, and no free oxygen escapes from the converter. Blast is assumed to be dry.

Requirements:

- (1) What weight of oxygen is needed during the blow.
- (2) How many cubic meters of air, at standard conditions, will be needed.
- (3) What will be the average composition of the gases.

Reactions:



Oxygen needed:

C to CO^2 100 kilos.	$\times 32/12 = 266.7$	kilos.
C to CO 200	$\times 32/24 = 266.7$	"
Mn to MnO 50	$\times 32/110 = 14.5$	"
Si to SiO^2 150	$\times 32/28 = 171.4$	"
Fe to FeO 500	$\times 32/112 = 142.8$	"
Total	862.1	"
Nitrogen accompanying this	= 2873.7	"
Air needed	3735.8	"

$$\text{Volume of air} \dots = \frac{3735.8}{1.293} = 2889.3 \text{ cubic meters} \quad (2)$$

Volume of products of combustion:

$$CO^2 = 100 + 266.7 = 366.7 \text{ kilos} = \frac{366.7}{1.98} = 185.2 \text{ cu. m.}$$

$$CO = 200 + 266.7 = 466.7 \text{ kilos} = \frac{466.7}{1.26} = 370.4 \text{ cu. m.}$$

$$N^2 = \frac{2873.7}{1.26} = 2280.7 \text{ "}$$

$$\text{Total volume} \dots \dots \dots \frac{2836.3}{\text{ "}}$$

Percentage composition by volume:

CO ²	6.5 per cent.
CO	13.1 " "
N ²	80.4 " "

CHAPTER II.

THE APPLICATIONS OF THERMOCHEMISTRY.

The ordinary interpretation of the chemical equation by weight gives us the quantitative relations governing the reactions of substances upon each other, when the reaction proceeds to a finish. Unfortunately, much chemical instruction, as given in our elementary schools, and even in some of the higher ones, stops with the consideration of the weight relations and does not proceed to those equally important relations, the energetics of chemical reactions. In most of the reactions which occur in practical metallurgy, the quantity of the combustible used, or, more broadly, the amount of energy in the form of heat or electrical energy, necessary for producing the reactions desired, is the controlling factor regulating the practicability or impracticability, the commercial success or failure, of the process.

The relative values of fuels, the manufacture and utilization of gas, the principles of the regenerative furnace, the Bessemer process, electric reduction, and a host of metallurgical processes, depend essentially on the realization and utilization of chemical energy, and the only way to become conversant with the amounts of energy involved or evolved in these operations is to understand thoroughly the thermochemistry of the reactions concerned.

THERMOCHEMICAL NOMENCLATURE

The heat evolved when compounds are formed from the elements (in a few cases heat is absorbed) is determined experimentally by the use of the calorimeter. This branch is sometimes called "chemical calorimetry;" it is practically a department of experimental physics. The data obtained give the heat evolved for the total change from the components at room temperature to the resulting products, at room tem-

perature (or very near to it), and may be expressed per unit of weight of either component or of the substance formed. Thus, if carbon is burned in a calorimeter to carbonic acid gas, CO^2 , the heat evolved may be reported or expressed as

8100 gram calories per gram of carbon burnt.

Or, 3037 gram calories per gram of oxygen used

Or, 2209 gram calories per gram of CO^2 formed.

Of these three methods of expressing the results, the first is the more often used, especially by the physicist.

The chemist, however, finds it often more convenient and logical to express these heats of combination per formula weight of the substances combining and of product formed. *E.g.*, In the case of CO^2 , which contains 12 parts of carbon and 32 of oxygen in 44 of the gas, the chemist would write,

$$(\text{C}, \text{O}^2) = 97,200,$$

meaning thereby that when 12 grams of carbon is burnt by 32 grams of oxygen, forming 44 grams of carbon dioxide, there is evolved 97,200 gram-calories. These are the laboratory units; for practical purposes, we call the weights kilograms and the heat units kilogram-calories (gram-calories are abbreviated to "cal."; kilogram-calories to "Cal."). Ostwald, in his thermochemical tables writes $(\text{C}, \text{O}^2) = 972 \text{ K}$, where K represents a unit 100 times as large as a gram-calorie, if weights are taken as being grams. Berthelot writes $(\text{C}, \text{O}^2) = 97.2$, where the heat units are kilogram-calories, if the weights concerned are taken as grams. Both these methods of expression are liable to cause confusion; the writer prefers to follow the older thermochemists (Hess, Naumann) and to use the larger number, *e.g.*, 97,200, which then means gram-calories, if weights are taken in grams (laboratory units), and kilogram-calories, if weights are taken in kilograms (practical units).

If it is desired to work in "British Thermal Units" (1 B. T. U. is the heat needed to raise one pound of water one degree Fahrenheit), the weights represented by the formula may be called pounds, and then the expression is as follows:

$$(\text{C}, \text{O}^2) = [97,200 \times 9/5] = 174,960 \text{ B. T. U.}$$

The factor $9/5$ is simply the relation of 1°C. to 1°F. ; the

reasoning is, of course, that if the combustion of 12 kilograms of carbon evolves 97,200 kilogram calories, or would heat 97,200 kilograms of water 1° C., that the combustion of 12 pounds of carbon would heat 97,200 pounds of water 1° C., or 174,960 pounds 1° F. From the equation as thus expressed and interpreted, the heat of combination per pound of carbon burnt, or of oxygen used, or of product formed, may be found in B. T. U. by dividing 174,960 by 12, 16 or 44, respectively.

Since it is very inconvenient, as well as unscientific, to have the two unrelated heat units, with their resulting double sets of experimental data, I strongly recommend the use of the metric data and metric Centigrade heat unit. It is, however, sometimes convenient, when all the data of a problem are given in English weights, to use as the unit of heat the "pound -1° C.," or the heat required to raise the temperature of one pound of water 1° C. This may be called the "pound cal.," as distinguished from the B. T. U. The advantage of using it is that all the experimental data of the metric system units are at once transferable to the English weights. *E.g.*, $(C, O^2) = 97,200$ pound cal., if the weights concerned in the formula (12, 32, 44) are called pounds.

The thermochemist gives all his experimental data in the form above explained, and we will now give all the important thermochemical data known which are useful in metallurgical calculations, *the data being for the reactions beginning and ending at 15° C. (60° F.)*:

THERMOCHEMICAL DATA.

HEAT OF FORMATION OF OXIDES.

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In dilute Solution.</i>
(Mg, O)	24 + 16 = 40	143,400	148,800
(Ba, O)	137 + 16 = 153	133,400	161,500
(Ca, O)	40 + 16 = 56	131,500	149,600
(Sr, O)	87 + 16 = 103	131,200	158,400
(Al ² , O ³)	54 + 48 = 102	392,600
(Na ² , O)	46 + 16 = 62	100,900	155,900
(K ² , O)	78 + 16 = 94	98,200	165,200
(Si, O ²)	28 + 32 = 60	180,000
(Mn, O)	55 + 16 = 71	90,900
(B ² , O ³)	22 + 48 = 70	272,600	279,900

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In dilute Solution.</i>	
(Zn, O)	65 + 16 = 81	84,800	
(Mn ³ , O ⁴)	165 + 64 = 229	328,000	
(P ² , O ⁵)	62 + 80 = 142	365,300	
(Sn, O)	118 + 16 = 134	70,700	
(Sn, O ²)	118 + 32 = 150	141,300	
(CO, O)	28 + 16 = 44	68,040	73,940	
(H ² , O)	2 + 16 = 18	{ 70,400 (solid) { 69,000 (liquid) { 58,060 (gas)	
(Fe ³ , O ⁴)	168 + 64 = 232		270,800
(Cd, O)	112 + 16 = 128		66,300
(Fe, O)	56 + 16 = 72	65,700	
(Fe ² , O ³)	112 + 48 = 160	195,600	
(Co, O)	59 + 16 = 75	64,100	
(Mr, O ²)	55 + 32 = 87	125,300	
(Ni, O)	58.5 + 16 = 74.5	61,500	
(Sb ² , O ³)	240 + 48 = 288	166,900	
(As ² , O ³)	150 + 48 = 198	156,400	148,900	
(Pb, O)	207 + 16 = 223	50,800	
(C, O ²)	12 + 32 = 44	97,200 (gas)	103,100	
(Bi ² , O ³)	416 + 48 = 464	139,200	
(Sb ² , O ⁵)	240 + 80 = 320	231,200	
(As ² , O ⁵)	150 + 80 = 230	219,400	225,400	
(Cu ² , O)	127.2 + 16 = 143.2	43,800	
(Tl ² , O)	408 + 16 = 424	42,800	39,700	
(Cu, O)	63.6 + 16 = 79.6	37,700	
(Ba, O ²)	137 + 32 = 169	145,500	
(S, O ²)	32 + 32 = 64	69,260 (gas)	77,600	
(Pb, O ²)	207 + 32 = 239	63,400	
(S, O ³)	32 + 48 = 80	91,900	141,000	
(Tl ² , O ³)	408 + 48 = 456	87,600	
(C, O)	12 + 16 = 28	29,160 (gas)	
(Hg ² , O)	400 + 16 = 416	22,200	
(Hg, O)	200 + 16 = 216	21,500	
(Te, O ²)	125.5 + 32 = 157.5	78,300	
(Pd, O)	106 + 16 = 122	21,000	
(Pt, O)	195 + 16 = 211	17,000 (?)	
(Ag ² , O)	216 + 16 = 232	7,000	
(Au ² , O ³)	394 + 48 = 442	-11,500	

See page 202a for this table in different form, expressed per unit weights of substances concerned.

HEAT OF FORMATION OF HYDRATES.

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In Dilute Solution.</i>
(Li, O, H)	$7+16+1=24$	112,300	118,100
(Mg, O ² , H ²)	$24+32+2=58$	217,800
(Sr, O ² , H ²)	$87+32+2=121$	217,300	227,400
(Ca, O ² , H ²)	$40+32+2=74$	215,600	219,500
(K, O, H)	$39+16+1=56$	104,600	117,100
(Na, O, H)	$23+16+1=40$	102,700	112,500
(N, H ⁵ , O)	$14+5+16=35$	88,800	90,000
(Al, O ³ , H ³)	$27+48+3=78$	301,300
(H, O, H)	$1+16+1=18$	70,400 (solid)
		69,000 (liquid)
		58,060 (gas)
(Tl, O, H)	$204+16+1=221$	57,400	54,300
(Bi, O ³ , H ³)	$208+48+3=259$	171,700
(Zn, O ² , H ²)	$65+32+2=99$	83,500
(Te, O ² , H ²)	$127+32+2=161$	78,300
(Te, O ³ , H ³)	$127+48+3=178$	99,500
(Se, O ² , H ²)	$79+32+2=113$	52,400	51,500
(Se, O ³ , H ³)	$79+48+3=130$	79,300
(Tl, O ³ , H ³)	$204+48+3=255$	43,800

HEAT OF FORMATION OF SULPHIDES.

(Li ² , S)	$14+32=46$	115,400
(K ² , S)	$78+32=110$	103,500	113,500
(Ba, S)	$137+32=169$	102,900	109,800
(Sr, S)	$87+32=119$	99,300	106,700
(Ca, S)	$40+32=72$	94,300	100,600
(Na ² , S)	$46+32=78$	89,300	104,300
(Mg, S)	$24+32=56$	79,400
(K, S ²)	$39+64=103$	59,300	59,700
(Na, S ²)	$23+64=87$	49,500	54,400
(Mn, S)	$55+32=87$	45,600
(Zn, S)	$65+32=97$	43,000
(Al ² , S ³)	$54+96=150$	126,400
(N, H ⁵ , S)	$14+5+32=51$	40,000	36,700
(Cd, S)	$112+32=144$	34,400
(B ² , S ³)	$22+96=118$	75,800

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation</i>	<i>In dilute Solution.</i>
(Fe, S)	56 + 32 = 88	24,000
(Co, S)	59 + 32 = 91	21,900
(Tl ² , S)	204 + 32 = 236	21,600
(Cu ² , S)	127.2 + 32 = 159.2	20,300
(Pb, S)	207 + 32 = 239	20,200
(Si, S ²)	28 + 64 = 92	40,000
(Ni, S)	58.5 + 32 = 90.5	19,500
(Sb, ² S ³)	240 + 96 = 336	34,400
(Hg, S)	200 + 32 = 232	10,600
(Cu, S)	63.6 + 32 = 95.6	10,100
(H ² , S)	2 + 32 = 34	4,800 (gas)	9,500
(Ag ² , S)	216 + 32 = 248	3,000
(C, S ²)	12 + 64 = 76	-25,400 (gas)
		-19,000 (liquid)
(I, S)	127 + 32 = 159	0,000

HEAT OF FORMATION OF SELENIDES.

(Li ² , Se)	14 + 79 = 93	83,000	93,700
(K ² , Se)	78 + 79 = 157	79,600	87,900
(Ba, Se)	137 + 79 = 216	69,900
(Sr, Se)	87 + 79 = 166	67,600
(Na ² , Se)	46 + 79 = 125	60,900	78,600
(Ca, Se)	40 + 79 = 119	58,000
(Zn, Se)	65 + 79 = 144	30,300
(Cd, Se)	112 + 79 = 191	23,700
(Mn, Se)	55 + 79 = 134	22,400
(N, H ⁵ , Se)	14 + 5 + 79 = 98	17,800	12,800
(Cu, Se)	63.6 + 79 = 142.6	17,300
(Pb, Se)	207 + 79 = 286	17,000
(Fe, Se)	56 + 79 = 135	15,200
(Ni, Se)	58.5 + 79 = 137.5	14,700
(Co, Se)	59 + 79 = 138	13,900
(Tl ² , Se)	408 + 79 = 487	13,400
(Cu ² , Se)	127.2 + 79 = 206.2	8,000
(Hg, Se)	200 + 79 = 279	6,300
(Ag ² , Se)	216 + 79 = 295	2,000
(H ² , Se)	2 + 79 = 81	-25,100 (gas)	-15,800
(N, Se)	14 + 79 = 93	-42,300

HEAT OF FORMATION OF TELLURIDES.

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In dilute Solution.</i>
(Zn, Te)	65 + 126 = 191	31,000
(Cd, Te)	112 + 126 = 138	16,600
(Co, Te)	59 + 126 = 185	13,000
(Fe, Te)	56 + 126 = 182	12,000
(Ni, Te)	58.5 + 126 = 184.5	11,600
(Ti ² , Te)	408 + 126 = 534	10,600
(Cu ² , Te)	127.2 + 126 = 253.2	8,200
(Pb, Te)	207 + 126 = 333	6,200
(H ² , Te)	2 + 126 = 128	-34,900 (gas)

HEAT OF FORMATION OF ARSENIDES.

(H ³ , As)	3 + 75 = 78	-44,200 (gas)
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HEAT OF FORMATION OF ANTIMONIDES.

(H ³ , Sb)	3 + 120 = 123	-86,800 (gas)
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HEAT OF FORMATION OF PHOSPHIDES.

(Mn ³ , P ²)	165 + 62 = 227	70,900
(H ³ , P)	3 + 31 = 34	4,900 (gas)
(Fe, P)	56 + 39 = 95	nearly zero.

HEAT OF FORMATION OF NITRIDES.

(H ³ , N)	3 + 14 = 17	12,200 (gas)	21,000
		16,600 (liquid)
(Ba ³ , N ²)	411 + 28 = 439	149,400
(Li ³ , N)	21 + 14 = 35	49,500
(K, H ³ , N)	39 + 3 + 14 = 56	30,700

HEAT OF FORMATION OF METALLIC HYDRIDES.

(Sr, H ²)	87 + 2 = 89	38,400
(Ba, H ²)	137 + 2 = 139	37,500
(Pt ¹⁰ , H)	1950 + 1 = 1,951	14,200
(Pd ¹⁵ , H)	1590 + 1 = 1,591	4,600
(Si, H ⁴)	28 + 4 = 32	-6,700 (gas)

HEAT OF FORMATION OF HYDROCARBONS.
(All formed in state of gas, unless otherwise specified.)

<i>Name.</i>	<i>Formula</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>
Methane (marsh gas)	(C, H ⁴)	12 + 4 = 16	22,250
Ethane (ethylene hydride).....	(C ² , H ⁶)	24 + 6 = 30	26,650
Propane (propylene hydride)	(C ³ , H ⁸)	36 + 8 = 44	33,850
Ethylene (olefiant gas)	(C ² , H ⁴)	24 + 4 = 28	-11,250
Propylene.	(C ³ , H ⁶)	36 + 6 = 42	- 6,050
Toluene	(C ⁷ , H ⁸)	84 + 8 = 92	- 5,650 (liquid)
Benzene.....	(C ⁶ , H ⁶)	72 + 6 = 78	{ - 750 (liquid)
			{ - 7 950 (gas)
Turpentine	(C ¹⁰ H ¹⁶)	120 + 16 = 136	{ 7 550 (liquid)
			{ - 1,850 (gas)
Naphthaline	(C ¹⁰ H ⁸)	120 + 8 = 128	{ -19,450 (solid)
			{ -24,050 (liquid)
Anthracene.. ..	(C ¹⁴ , H ¹⁰)	168 + 10 = 178	-39 050 (solid)
Acetylene.	(C ² , H ²)	24 + 2 = 26	-54,750
Methyl-alcohol (wood spirit).....	(C, H ⁴ , O)	12 + 4 + 16 = 32	{ 65,050 (liquid)
			{ 56,650 (gas)
Ethyl-alcohol (alcohol).....	(C ² , H ⁶ , O)	24 + 6 + 16 = 46	{ 73 250 (liquid)
			{ 63,150 (gas)
Acetone.....	(C ³ , H ⁶ , O)	36 + 6 + 16 = 58	{ 69,650 (liquid)
			{ 62,150 (gas)

HEAT OF FORMATION OF CARBIDES.

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In dilute Solution.</i>
(Al ⁴ , C ³)	108 + 36 = 144	232,000
(Mn, C ²)	55 + 24 = 79	114,400 (Pontherie)...	
(Mn, C ³)	55 + 36 = 91	9,900 (Berthelot) ...	
(Mn ³ , C)	165 + 12 = 177	10,400 (Le Chatelier) .	
(Fe ³ , C)	168 + 12 = 180	8,460
(Ca, C ²)	40 + 24 = 64	-6,250
(Na, C)	23 + 12 = 35	-4,400
(Li, C)	7 + 12 = 19	-5,750
(N ² , C ²)	28 + 24 = 52	-73,000 (gas)	-67,100
(Ag, C)	108 + 12 = 120	-43,575

HEAT OF FORMATION OF SILICIDES.

(Mn ⁷ , Si ²)	385 + 56 = 441	47,400
(H ⁴ , Si)	4 + 28 = 32	-6,700 (gas)

HEAT OF FORMATION OF FLUORIDES.

(Sr, F ²)	87 + 38 = 125	224,020
(Ba, F ²)	137 + 38 = 175	224,000	221,500
(Li, F)	7 + 19 = 26	116,880
(K, F)	39 + 19 = 58	110,000	113,600
(Ca, F ²)	40 + 38 = 78	216,450
(Mg, F ²)	24 + 38 = 62	209,500
(Na, F)	23 + 19 = 42	109,720	109,120
(N; H ⁴ , F)	14 + 4 + 19 = 37	101,250	99,750
(Al, F ³)	27 + 57 = 84	275,220
(B, F ³)	11 + 57 = 68	219,345
(Mn, F ²)	55 + 38 = 93	153,310
(Zn, F ²)	65 + 38 = 103	138,220
(Si, F ⁴)	28 + 76 = 104	275,920 (gas)
(Fe, F ²)	56 + 38 = 94	125,220
(Cd, F ²)	112 + 38 = 150	121,720
(Co, F ²)	59 + 38 = 97	120,340
(Ni, F ²)	58.5 + 38 = 96.5	118,980
(Fe, F ³)	56 + 57 = 113	164,940
(Tl, F)	204 + 19 = 223	54,405
(Pb, F ²)	207 + 38 = 245	101,600
(H, F)	1 + 19 = 20	38,500 (gas)	50,300
(Sb, F ³)	120 + 57 = 177	136,680

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In dilute Solution.</i>
(Cu, F ²)	63.6 + 38 = 101.6	88,160
(Ag, F)	108 + 19 = 127	22,070	25,470

HEAT OF FORMATION OF CHLORIDES.

(K, Cl)	39 + 35.5 = 74.5	105,700	101,200
(Be, Cl ²)	9 + 71 = 80	155,000	199,500
(Ba, Cl ²)	137 + 71 = 208	197,100	198,300
(Na, Cl)	23 + 35.5 = 58.5	97,900	96,600
(Li, Cl)	7 + 35.5 = 42.5	93,900	102,300
(Sr, Cl ²)	87 + 71 = 158	184,700	195,850
(Ca, Cl ²)	40 + 71 = 111	169,900	187,400
(N, H ¹ , Cl)	14 + 4 + 35.5 = 63.5	76,800	72,800
(Mg, Cl ²)	24 + 71 = 95	151,200	187,100
(Al, Cl ³)	27 + 106.5 = 133.5	161,800	238,100
(Mn, Cl ²)	55 + 71 = 126	112,000	128,000
(Zn, Cl ²)	65 + 71 = 136	97,400	113,000
(Tl, Cl)	204 + 35.5 = 239.5	48,600	38,400
(Cd, Cl ²)	112 + 71 = 183	93,700	96,400
(Pb, Cl ²)	207 + 71 = 278	83,900	77,900
(Fe, Cl ²)	56 + 71 = 127	82,200	100,100
(Sn, Cl ²)	118 + 71 = 189	80,900
(Co, Cl ²)	59 + 71 = 130	76,700	95,000
(Ni, Cl ²)	58.5 + 71 = 129.5	74,700	93,900
(Cu, Cl)	63.5 + 35.5 = 99	35,400
(Sn, Cl ⁴)	118 + 142 = 260	129,800 (liquid)
(Fe, Cl ³)	56 + 106.5 = 162.5	96,150	127,850
(Hg, Cl)	200 + 35.5 = 235.5	31,320
(Sb, Cl ³)	120 + 106.5 = 226.5	91,400
(Bi, Cl ³)	208 + 106.5 = 314.5	90,800
(Si, Cl ⁴)	28 + 142 = 170	128,800 (gas)
(B, Cl ³)	11 + 106.5 = 117.5	89,100 (gas)
(Ag, Cl)	108 + 35.5 = 143.5	29,000
(Hg, Cl ²)	200 + 71 = 271	53,300	50,300
(Cu, Cl ²)	63.6 + 71 = 134.6	51,400	62,500
(As, Cl ³)	75 + 106.5 = 181.5	71,500
(H, Cl)	1 + 35.5 = 36.5	22,000	39,400
(Sb, Cl ⁵)	120 + 177.5 = 297.5	104,500 (liquid)
(Pd, Cl ²)	106 + 71 = 177	40,500

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In dilute Solution.</i>
(Pt, Cl ⁴)	195 + 142 = 337	60,200	79,800
(Au, Cl ³)	197 + 106.5 = 303.5	22,800	27,200
(Au, Cl)	197 + 35.5 = 232.5	5,800

HEAT OF FORMATION OF CARBONATES.

(Ba, C, O ³)	137 + 12 + 48 = 197	286,300
(K ² , C, O ³)	78 + 12 + 48 = 138	282,100	288,600
(Sr, C, O ³)	87 + 12 + 48 = 147	281,400
(Ca, C, O ³)	40 + 12 + 48 = 100	273,850
(Na ² , C, O ³)	46 + 12 + 48 = 106	273,700	279,300
(Mg, C, O ³)	24 + 12 + 48 = 84	269,900
(Mn, C, O ³)	55 + 12 + 48 = 115	210,300
(N, H ⁵ , C, O ³)	14 + 5 + 12 + 48 = 79	208,600	202,300
(Zn, C, O ³)	65 + 12 + 48 = 125	197,500
(Fe, C, O ³)	56 + 12 + 48 = 116	187,800
(Cd, C, O ³)	112 + 12 + 48 = 172	183,200
(Pb, C, O ³)	207 + 12 + 48 = 267	170,000
(Cu, C, O ³)	63.6 + 12 + 48 = 123.6	146,100
(Ag ² , C, O ³)	216 + 12 + 48 = 276	123,800

HEAT OF FORMATION OF BICARBONATES.

(K, H, C, O ³)	39 + 1 + 12 + 48 = 100	233,300	228,000
(Na, H, C, O ³)	23 + 1 + 12 + 48 = 84	227,000	222,700

HEAT OF FORMATION OF NITRATES.

(K, N, O ³)	39 + 14 + 48 = 101	119,000	110,700
(Na, N, O ³)	23 + 14 + 48 = 85	110,700	106,000
(Zn, N ² , O ⁶)	65 + 28 + 96 = 187	131,700
(Pb, N ² , O ⁶)	207 + 28 + 96 = 331	105,400	98,200
(Cu, N ² , O ⁶)	63.5 + 28 + 96 = 187.5	81,300
(H, N, O ³)	1 + 14 + 48 = 63	34,400 gas	48,800
(Ag, N, O ³)	108 + 14 + 48 = 170	28,700	23,000

HEAT OF FORMATION OF PHOSPHATES.

(Ca ³ , P ² , O ⁸)	120 + 62 + 128 = 310	919,200
(Mg ³ , P ² , O ⁸)	72 + 62 + 128 = 262	910,600
(Na ³ , P, O ⁴)	69 + 31 + 64 = 164	452,400

HEAT OF FORMATION OF SILICATES.

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In dilute Solution.</i>
(Ba, Si, O ³)	137 + 28 + 48 = 213	328,100
(Ca, Si, O ³)	40 + 28 + 48 = 116	329,350
(Ca ² , Si, O ⁴)	80 + 28 + 64 = 172	471,300
(Ca ³ , Si, O ⁵)	120 + 28 + 80 = 228	603,050
(Sr, Si, O ³)	87 + 28 + 48 = 163	329,100
(Al ² , Si ² , O ⁷)	54 + 56 + 112 = 222	767,500
(Li ² , Si, O ³)	14 + 28 + 48 = 90	347,100 (?)
(Na ² , Si, O ³)	46 + 28 + 48 = 122	326,100
(Ca ³ , Al ² , Si ² , O ¹⁰)	120 + 54 + 56 + 160 = 390	1,195,550
(H ⁴ , Al ² , Si ² , O ⁹)	4 + 54 + 56 + 144 = 258	927,420
(Mn, Si, O ³)	55 + 28 + 48 = 131	276,300
(Fe, Si, O ³)	56 + 28 + 48 = 132	254,600

HEAT OF FORMATION OF ALUMINATES.

(Ca, Al ² , O ⁴)	40 + 54 + 64 = 158	524,550
(Ca ² , Al ² , O ⁵)	80 + 54 + 80 = 214	658,900
(Ca ³ , Al ² , O ⁶)	120 + 54 + 96 = 270	789,050

HEAT OF FORMATION OF SULPHATES.

(K ² , S, O ⁴)	78 + 32 + 64 = 174	344,300	337,700
(Ba, S, O ⁴)	137 + 32 + 64 = 233	339,400
(Li ² , S, O ⁴)	14 + 32 + 64 = 110	333,500	339,600
(Sr, S, O ⁴)	87 + 32 + 64 = 183	330,200
(Na ² , S, O ⁴)	46 + 32 + 64 = 142	328,100	328,500
(Ca, S, O ⁴)	40 + 32 + 64 = 136	317,400	321,800
(Mg, S, O ⁴)	24 + 32 + 64 = 120	300,900	321,100
(Al ² , S ³ , O ¹²)	54 + 96 + 192 = 342	879,700
(N ² , H ⁸ , S, O ⁴)	28 + 8 + 32 + 64 = 132	283,500	281,100
(Mn, S, O ⁴)	55 + 32 + 64 = 151	249,400	263,200
(Zn, S, O ⁴)	65 + 32 + 64 = 161	229,600	248,000
(Fe, S, O ⁴)	56 + 32 + 64 = 152	234,900
(Co, S, O ⁴)	59 + 32 + 64 = 155	228,900
(Ni, S, O ⁴)	58.5 + 32 + 64 = 154.5	228,700
(Fe ² , S ³ , O ¹²)	112 + 96 + 192 = 400	650,500
(Ti ² , S, O ⁴)	408 + 32 + 64 = 504	221,800	213,500
(Cd, S, O ⁴)	112 + 32 + 64 = 208	219,900	231,600
(Pb, S, O ⁴)	207 + 32 + 64 = 303	215,700

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In dilute Solution.</i>
(H ² , S, O ⁴)	2+32+64 = 98	192,200	210,200
(Cu, S, O ⁴)	63.6+32+64 = 159.6	181,700	197,500
(Hg ² , S, O ⁴)	400+32+64 = 496	175,000
(Ag ² , S, O ⁴)	216+32+64 = 312	167,100	162,600
(Hg, S, O ⁴)	200+32+64 = 296	165,100

HEAT OF FORMATION OF BI-SULPHATES.

(K, H, S, O ⁴)	39+1+32+64 = 136	276,100	272,900
(Na, H, S, O ⁴)	23+1+32+64 = 120	269,100	268,300
(N, H ⁵ , S, O ⁴)	14+5+32+64 = 115	244,600	245,100
(H H, S, O ⁴)	1+1+32+64 = 98	192,200	210,200

HEAT OF FORMATION OF BORATES.

(Na ² , B ⁴ , O ⁷)	46+44+112 = 202	748,100	758,300
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HEAT OF FORMATION OF CYANIDES.

(Ca, C ² , N ²)	40+ 24+ 28 = 92	41,650
(K, C, N)	39+ 12+ 14 = 65	33,450	30,250
(Na, C, N)	23+ 12+ 14 = 49	25,950	25,450
(K, Ag, C ² , N ²)	39+108+ 24+ 28 = 199	13,700	5,350
(Fe ⁷ , C ¹⁸ , N ¹⁸)	392+216+252 = 860	-256,700
(Zn, C ² , N ²)	65+ 24+ 28 = 117	-24,550
(Cd, C ² , N ²)	112+ 24+ 28 = 164	-31,850
(Cu, C, N)	63.6+ 12+ 14 = 89.6	-20,375
(Pd, C ² , N ²)	106+ 24+ 28 = 158	-49,250
(H, C, N)	1+ 12+ 14 = 27	-27,150 _{gas}	-21050
(Hg, C ² , N ²)	200+ 24+ 28 = 252	-59,150

HEAT OF FORMATION OF CYANATES.

(K, C, N, O)	39+12+14+16 = 81	105,850	100,650
(Na, C, N, O)	23+12+14+16 = 65	105,050	100,250
(Ag, C, N, O)	108+12+14+16 = 150	26,450

HEAT OF FORMATION OF FERROCYANIDES.

(K ⁴ , Fe, C ⁶ , N ⁶)	156+56+72+84 = 368	157,300	145,300
(H ⁴ , Fe, C ⁶ , N ⁶)	4+56+72+84 = 216	-102,000	-101,500
(K ³ , Fe, C ⁶ , N ⁶)	117+56+72+84 = 329	129,600	100,800
(H ³ , Fe, C ⁶ , N ⁶)	3+56+72+84 = 215	-127,400

HEAT OF FORMATION OF AMALGAMS.

<i>Formula.</i>	<i>Molecular Weights.</i>	<i>Molecular Heat of Formation.</i>	<i>In dilute Solution.</i>
(Hg ¹² , K)	2,400 + 39 = 2,439	34,600	25,600
(Hg ⁴ , K)	800 + 39 = 839	29,700	25,600
(Hg ⁶ , Na)	1,200 + 23 = 1,223	21,900	19,000
(Hg ^x , Au)	$x + 197 = 197 + x$	2,580
(Hg ^x , Ag)	$x + 108 = 108 + x$	2,470

HEAT OF FORMATION OF ALLOYS.

(Cu, Zn ²)	63.6 + 130 = 193.6	10,143
(Cu, Zn)	63.6 + 65 = 128.6	5,783
(Cu ³ , Al)	190.8 + 27 = 217.8	26,910
(Cu ² , Al)	127.2 + 27 = 154.2	21,278
(Cu ³ , Al ²)	190.8 + 54 = 244.8	17,395
(Cu, Al)	63.6 + 27 = 90.6	1,887
(Cu ² , Al ³)	127.2 + 81 = 208.2	10,196
(Cu, Al ²)	63.6 + 54 = 117.6	-6,738

CHAPTER III.

THE USE OF THE THERMOCHEMICAL DATA.

SIMPLE COMBINATIONS.

If the problem is the simple calculation of how much heat is evolved in the combination of a given weight of one element with another, the factors needed, the heat evolved per unit weight of substance combining, are obtained by a simple division from the thermochemical data given. Thus, suppose the question to be the total heat evolved in Problem 3, in the oxidation in a Bessemer converter of

100 kilos. of carbon to carbonic oxide.

200 kilos. of carbon to carbonous oxide.

50 kilos. of manganese to MnO.

150 kilos. of silicon to SiO².

500 kilos. of iron to FeO.

The solution would be

$$100 \times \frac{97,200}{12} = 100 \times 8100 = 810,000 \text{ Calories.}$$

$$200 \times \frac{29,160}{12} = 200 \times 2430 = 486,000 \quad "$$

$$50 \times \frac{90,900}{55} = 50 \times 1653 = 82,650 \quad "$$

$$150 \times \frac{180,000}{28} = 150 \times 6429 = 964,350 \quad "$$

$$500 \times \frac{65,700}{56} = 500 \times 1173 = \frac{586,500}{\text{Total } 2,929,500} \quad "$$

COMPLEX COMBINATIONS.

If the problem is a step more complex, that is, includes the combination of compounds with each other to form a more

complex compound, the molecular weights are still our guide, together with the thermochemical data given. If, for instance, the question above solved is complicated by the further requirement, to add the heat evolved by the formation of the slag, that is, of the MnO and FeO with SiO² to form silicate, we may calculate the heat of union of FeO and MnO with SiO² as follows:

	(Mn, Si, O ³) = 276,300 Calories.
But	(Mn, O) = 90,900 “
and	(Si, O ²) = 180,000 “
therefore	(MnO, SiO ²) = 5,400 “
	or, per kilo. of MnO = $\frac{5,400}{71} = 76$ Calories.

Similarly

	(Fe, Si, O ³) = 254,600 Calories.
	(Fe, O) = 65,700 “
	(Si, O ²) = 180,000 “
	(FeO, SiO ²) = 8,900 “
	per kilo. of FeO = $\frac{8,900}{72} = 124$ Calories.

Therefore the additional heat of formation of the slag may be

Wt. MnO =	64.5 kilos. ×	76 =	4,902 Calories.
Wt. FeO =	642.8 “	× 124 =	79,707 “
		Sum =	84,609 “

Similar principles of calculation apply to all the oxygen-containing salts. Thus, if from the heat of formation of any sulphate we subtract the heat of formation of SO³, and also of the metallic oxide present, the residue is the heat of combination of the metallic oxide with SO³,—the weights involved being always those represented by the formulæ. Thus, calling MO any metallic oxide, we may express the principle as follows:

(MO, SiO ²)	=	(M, Si, O ³)	—	(M, O)	—	(Si, O ²)
(MO, SO ³)	=	(M, S, O ³)	—	(M, O)	—	(S, O ³)
(MO, CO ²)	=	(M, C, O ³)	—	(M, O)	—	(C, O ²)
(3MO, P ² O ⁵)	=	(M ³ , P ² , O ⁸)	—	3(M, O)	—	(P ² , O ⁵)
etc.		etc.				

Example.—What is the heat required to calcine limestone?

$$\begin{aligned}(\text{CaO}, \text{CO}^2) &= (\text{Ca}, \text{C}, \text{O}^3) - (\text{Ca}, \text{O}) - (\text{C}, \text{O}^2) \\ &= 273,850 - 131,500 - 97,200 \\ &= 45,150 \text{ Calories.}\end{aligned}$$

This is the heat required to split up CaCO^3 (100 parts) into CaO (56) and CO^2 (44); the heat required is therefore

$$\begin{aligned}45,150 \div 100 &= 451.5 \text{ Calories per kilo. of } \text{CaCO}^3 \text{ decomposed.} \\ 45,150 \div 44 &= 1026. \quad \text{“ “ “ } \text{CO}^2 \text{ driven off.} \\ 45,150 \div 56 &= 806. \quad \text{“ “ “ } \text{CaO remaining.}\end{aligned}$$

And either of these quantities may be used, according to convenience in working the problem.

DOUBLE DECOMPOSITIONS.

If the thermochemical problem involves the simultaneous decomposition of one or more substances and formation of one or more others, then the chemical equation should be written, and a thermochemical interpretation given of all the energy involved in the passage from starting compounds to products. Every chemical equation can be thus interpreted, if the heats of formation of all the compounds represented in it are known. We obtain the net energy of the reaction by assuming that all the substances used are resolved into their elements, and that all the products are formed from their elements; the first item is therefore to add together the heats of formation of all the substances used, starting with their elements, and by changing the algebraic sign of this sum we have the heat necessary to decompose the substances used into their elements; the second item is similarly found by adding together the heats of formation of all the substances formed; the difference between these two items is the net energy of the reaction. In making these summations, regard must, of course, be paid to the number of molecules of each substance concerned, as shown in the reaction (because the tabulated data are the heats of formation of one molecule only) and to the algebraic sign of the heats of formation.

Examples.—(a) What heat is evolved when dry ferric oxide is reduced by aluminium, in the Goldschmidt “Thermite” process?

$$\begin{array}{r|l}
 \text{Fe}^2\text{O}^3 + 2\text{Al} = & \text{Al}^2\text{O}^3 + 2\text{Fe} \\
 -195,600 & + 392,600 \\
 \hline
 & + 197,000 \text{ Calories.}
 \end{array}$$

(b) Write the equation showing the reaction of metallic sodium on water in excess:

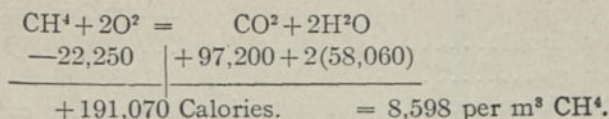
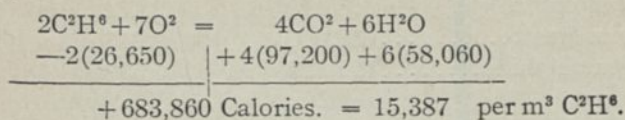
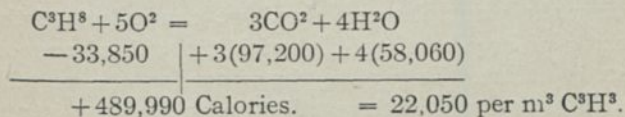
$$\begin{array}{r|l}
 2\text{H}^2\text{O} + 2\text{Na} = 2\text{NaOH} + \text{H}^2 + \text{aq. (excess water)} \\
 -2(69,000) & + 2(112,500) \\
 \hline
 -138,000 & + 225,000 \\
 \hline
 & + 87,000 \text{ Calories.}
 \end{array}$$

(c) What heat is evolved in the reaction of water on calcium carbide to form acetylene gas?

$$\begin{array}{r|l}
 \text{CaC}^2 + 2\text{H}^2\text{O} = \text{CaO}^2\text{H}^2 + \text{C}^2\text{H}^2 \\
 -(-6250) - 138,000 & + 215,600 + (-54,750) \\
 \hline
 -131,750 & + 160,850 \\
 \hline
 & + 29,100-
 \end{array}$$

The last case leaves out the very small heat of solution of the calcium hydrate which would normally go into solution. If such a large excess of water was used that all the calcium hydrate formed could dissolve, the heat of formation of the hydrate in dilute solution, 219,500 Calories, would be used, and the final result would be 33,000 Calories. The case is also very instructive, because it contains two compounds which are endothermic, that is, their heat of formation is negative, and therefore, as in the case of CaC^2 , heat is given out when it decomposes, while in the case of C^2H^2 heat is absorbed when it is formed.

(d) What are the heats of combustion of the gaseous hydrocarbons which form constituents of common fuels, expressed per cubic meter of gas burning, and with the water formed assumed remaining as vapor, uncondensed? To calculate these we write the equations of combustion, with water as gas, and find the sum total of heat evolved; since every molecule of gas burning represents 22.22 m³ of gas, we can, by a simple division, obtain the value sought.

Methane:*Ethane:**Propane:*

By applying these principles to all the hydrocarbons whose heat of formation has been given in the tables, we obtain the following useful table, water being considered as uncondensed and cold:

<i>Hydrocarbon.</i>	<i>Molecular Heat of Combustion.</i>		<i>Heat of Combustion of</i>	
	Calories.	1 m ³ (Calories)	1 ft ³ (B.T.U.)	
Methane (gas).....	191,070	8,598	966	
Ethane (gas).....	341,930	15,387	1728	
Propane (gas).....	489,900	22,050	2477	
Ethylene (gas).....	321,770	14,480	1627	
Propylene (gas).....	471,830	21,232	2385	
Toluene (liquid).....	906,990	
Benzene {	liquid.....	758,130
	gas.....	765,330	34,440	3869
Turpentine {	liquid.....	1,428,930
	gas.....	1,438,330	64,725	7271
Naphthaline {	solid.....	1,223,690
	liquid....	1,228,290	55,273	6209
Anthracine (solid).....	1,690,150	
Acetylene (gas).....	365,270	16,437	1846	
Methyl alcohol {	liquid..	148,270
	gas.....	156,670	7,050	799
Ethyl alcohol {	liquid...	295,330
	gas.....	305,430	13,744	1544

	<i>Molecular Heat of Combustion.</i>	<i>Heat of Combustion of</i>	
Acetone	{ liquid..... 396,130
	{ gas..... 403,630	18,163	2040
(To the above we will add data for three other common gaseous fuels.)			
Carbonous oxide (gas)	68,040	3,062	344
Hydrogen (gas).....	58,060	2,613	293.5
Hydrogen sulphide.....	122,520	5,513	619

CALORIFIC POWER OF FUELS.

By using the principles explained we can calculate the calorific power of any combustible, with the aid of one or two simple assumptions. Regarding the water formed, we will consider in all ordinary metallurgical calculations that it remains uncondensed, thus putting it on the same footing as the other products of combustion. This amounts virtually to assuming that the latent heat of condensation of the vapor formed has not been generated in the furnace, an assumption which is quite justified if, as is almost always the case, the water formed inevitably escapes as vapor. If, in any special case, the products of combustion are in reality cooled down so far that the water does condense, then it would be proper to assume the higher calorific powers for the combustion of the hydrogen-containing materials, and thus a more accurate heat-balance of the furnace operation could be constructed. An instance of the latter might be the case of the partial combustion of a fuel in a gas producer, where the fuel gas is afterwards cooled before using, in order to condense from it ammonia water, etc. (Mond's producer). In this case, it is possible that some water formed by the partial combustion would be afterwards condensed, and to obtain a correct heat-balance-sheet of the producer it would be necessary to assume that this heat had also been generated. Such cases occur very rarely in metallurgical practice, and it is therefore recommended to always use the lower calorific values, assuming water vapor uncondensed and its latent heat of condensation not to have been generated—unless the conditions of the problem point plainly to the opposite course as correct. It is no more correct to charge against a furnace the latent heat of condensation of the

water vapor formed, than it would be to charge against it the latent heat of condensation of the carbonic oxide formed, if the conditions of practice are such that it is impossible to utilize in any useful manner either one of them. Those who persist in assuming that the latent heat of vaporization of the water formed by combustion is generated in and chargeable against the furnace, and then, of necessity, charge the same quantity against the heat carried off in the products of combustion, are in the great majority of cases adding to both sides of the balance sheet a quantity which cannot possibly be utilized, and are therefore distorting all the factors of heat generation and distribution. By thus abnormally increasing the sensible heat in the waste gases, they abnormally *decrease* the proportionate value of other items of heat distribution and utilization. I have dwelt on this matter at length, because it is of importance in furnaces using fuel, such as gas, rich in hydrogen; where, in some cases, the counting of the latent heat of condensation of the water vapor formed in the escaping gases, would perhaps *double* the apparent chimney loss, and give distorted values to the whole heat balance sheet. What we are after, in every case, are the real facts and figures as to the working of a furnace or operation, and we must therefore judge the operation by a theoretically perfect standard, it is true, but not by a theoretically impossible standard; *i.e.*, our standard must be the theoretically possible one under the practical conditions necessarily prevailing. A radical reform is very much needed in just this respect,—in the treatment of the latent heat of vaporization of the water formed—by writers on metallurgical processes and problems of combustion.

Problem 4.

A natural gas from Kokomo, Ind., contained by analysis: CH⁴ 94.16, H² 1.42, C²H⁴ 0.30, CO² 0.27, CO 0.55, O² 0.32, N² 2.80, H²S 0.18 per cent.

Required:

(1) What is its metallurgical calorific power per cubic meter and per cubic foot?

(2) Comparing it with coal, having a calorific power of 8,000 Calories, how much gas gives the same generation of heat as a metric ton of coal?

(3) If the natural gas costs \$0.15 per 1,000 cubic feet, at what price per metric ton would the coal furnish heating power at the same cost for fuel?

Solution.—*Requirement* (1) Heat of combustion of 1 cubic meter:

$$\begin{array}{r}
 \text{CH}_4 \ 0.9416 \times 8,598 = 8095.9 \text{ Calories.} \\
 \text{H}_2 \ 0.0142 \times 2,613 = 37.1 \quad \text{"} \\
 \text{C}_2\text{H}_4 \ 0.0030 \times 14,480 = 43.4 \quad \text{"} \\
 \text{CO} \ 0.0055 \times 3,062 = 16.8 \quad \text{"} \\
 \text{H}_2\text{S} \ 0.0018 \times 5,513 = 9.9 \quad \text{"} \\
 \hline
 \text{Total} = 8203.1 \quad \text{"}
 \end{array}$$

In British thermal units per cubic foot we have

$$\begin{array}{l}
 8,203.1 \times 3.967 \div 35.314 = \\
 8,203.1 \times 0.11233 = 921.5 \text{ B. T. U. per ft}^3 \text{ (1)}
 \end{array}$$

Requirement (2):

$$\begin{aligned}
 \frac{8000 \times 1000}{8,203.1} &= 975 \text{ m}^3 \\
 &= 34,450 \text{ ft}^3.
 \end{aligned}$$

If the ton of coal be taken as 2240 pounds, instead of the metric ton of 2204 pounds, the equivalent volume is

$$34,450 \times \frac{2240}{2204} = 35,013 \text{ ft}^3.$$

Requirement (3):

$$\frac{34,450}{1000} \times 0.15 = \$5.16\frac{3}{4} \text{ per metric ton.}$$

or, per ton of 2240 pounds,

$$\$5.16\frac{3}{4} \times \frac{2240}{2204} = \$5.25 \text{ per long ton.}$$

DULONG AND PETIT'S LAW.

When a solid or liquid carbonaceous fuel is to be burned, its calorific power may either be determined directly in a calorimeter (which is the best way, if carefully done), or may be calculated from its analysis. In case it is determined calori-

metrically, the weight of water produced per unit of fuel should be determined either in the same or by a separate experiment, and the latent heat of vaporization of this water subtracted from the calorimetric value of the fuel, in order to get its metallurgical, or practical, calorific power.

Example.—A coal gave 9215 calories per gram in the calorimeter, and its products of combustion gave up 0.45 grams of condensed water. What is its practical calorific power?

Taking the products cold, the heat of condensation per gram of water vapor may be taken as 606.5 calories (Regnault), and we therefore have obtained in the calorimeter

$$0.45 \times 606.5 = 273 \text{ Calories}$$

more than if the products were cold and water uncondensed. The practical calorific power is therefore

$$9215 - 273 = 8942 \text{ Calories per kilogram.}$$

Dulong and Petit's law, or method of calculation, is the statement that the calorific power of a fuel can be calculated from the amount of carbon, hydrogen, and oxygen it contains by assuming all the carbon free to burn, the oxygen to be all combined with hydrogen in the proportions of O^2 to $2H^2$ (32 to 4), and that the rest of the hydrogen is free to burn.

Example.—Taking the bituminous coal of Problem 1, containing carbon 73.60, hydrogen 5.30, nitrogen 1.70, sulphur 0.75, oxygen 10.00, moisture 0.60, ash 8.05, its calculated calorific power is per kilogram:

Carbon	0.7360	×	8100	=	5962	Calories.	
Hydrogen	0.0530						
	— 0.0125						
	=		0.0405	×	34,500	=	1397
							“ (water liquid)
Sulphur	0.0075	×	2196	=	17		“
			Total		7376		“

This calculation is made, however, on the assumption that all the water in the products is condensed to liquid, *i.e.*, not only the water formed by combustion of the free hydrogen, but also the already-formed H^2O containing the oxygen of the coal, as well as the moisture present to start with. To obtain

the practical calorific power by calculation we must subtract from the above-generated heat the latent heat of *all* the vapor of water in the products, as follows:

Moisture in coal.....	0.0060	kilos.
Moisture formed by combined hydrogen..	0.1125	“
Moisture formed by free hydrogen.....	0.3645	“
Total.....	<u>0.4830</u>	“

Latent heat of vaporization = $606.5 \times 0.4830 = 293$ Calories.

Practical calorific power, water all as vapor = 7104 Calories.

The values thus calculated are found to agree satisfactorily with the laboratory and the practical calorific powers of the fuels.

THE THEORETICAL TEMPERATURE OF COMBUSTION.

If we start with a cold fuel and cold air the maximum temperature which can be obtained by the combustion is simply that temperature to which the heat generated can raise the products of combustion, assuming that all that heat resides primarily in the products as sensible heat. This is then a problem in physics, in which we have a known amount of heat available, and the question is to what temperature it will raise the products of combustion. The problem is at once soluble when we know the mean specific heats of the products of combustion and their respective quantities.

Until a few years ago these specific heats at high temperatures were unknown, and very false results were obtained by assuming constant specific heats from ordinary temperatures up, and values were thus calculated which were known to be hundreds, and in some cases, thousands, of degrees too high. The most satisfactory values for the specific heats of the fixed gases and water vapor and carbonic oxide are those determined by Mallard and Le Chatelier, and their proper use has entirely solved the question of theoretical temperatures of combustion, and removed a positively disgraceful discrepancy between theory and practice. The specific heats of these gases increase with temperature, so that the actual specific heat of a cubic meter (measured at standard conditions) is, at the temperature t ,—

$$\text{for } \text{N}^2, \text{O}^2, \text{H}^2, \text{CO} \text{ —S} = 0.303 + 0.000054t.$$

$$\text{“ “ } \text{CO}^2 \text{—S} = 0.37 + 0.00044t$$

$$\text{“ “ } (\text{vapor}) \text{H}^2\text{O—S} = 0.34 + 0.00030t$$

For calculating the quantity of heat needed to raise the gas from 0° to t° , however, we need the mean specific heats, Sm , between 0° and t° . These are, of course, the above constants plus half the increase, viz.:

$$\text{for } \text{N}^2, \text{O}^2, \text{H}^2, \text{CO—Sm} = 0.303 + 0.000027t$$

$$\text{“ } \text{CO}^2 \text{—Sm} = 0.37 + 0.00022t$$

$$\text{“ } (\text{vapor}) \text{H}^2\text{O—Sm} = 0.34 + 0.00015t$$

and the quantity of heat needed to raise 1 cubic meter (at standard conditions) from 0° to t° is

$$\text{for } \text{N}^2 \text{ O}^2 \text{ H}^2, \text{CO—Q} (0-t) = 0.303t + 0.000027t^2$$

$$\text{“ } \text{CO}^2 \text{—Q} (0-t) = 0.37t + 0.00022t^2$$

$$\text{“ } \text{H}^2\text{O—Q} (0-t) = 0.34t + 0.00015t^2$$

or, finally, the quantity of heat needed to raise 1 cubic meter (measured at standard conditions) from t to t' is

$$\text{for } \text{N}^2, \text{O}^2, \text{H}^2, \text{CO—Q} (t'-t) = 0.303 (t'-t) + 0.000027 (t'^2 - t^2)$$

$$\text{“ } \text{CO}^2 \text{—Q} (t'-t) = 0.37 (t'-t) + 0.00022 (t'^2 - t^2)$$

$$\text{“ } \text{H}^2\text{O—Q} (t'-t) = 0.34 (t'-t) + 0.00015 (t'^2 - t^2)$$

And the mean specific heat, Sm , between any two temperatures is

$$\text{for } \text{N}^2 \text{ O}^2, \text{H}^2, \text{CO —Sm} (t'-t) = 0.303 + 0.000027 (t' + t)$$

$$\text{“ } \text{CO}^2 \text{—Sm} (t'-t) = 0.37 + 0.00022 (t' + t)$$

$$\text{“ } \text{H}^2\text{O —Sm} (t'-t) = 0.34 + 0.00015 (t' + t)$$

Examples:

(1) What is the temperature of the hottest part of the oxygen-hydrogen blowpipe flame?

According to the equation $2\text{H}^2 + \text{O}^2 = 2\text{H}^2\text{O}$, the hydrogen gas forms an equal volume of water vapor. (Equal numbers of molecules.) The heat of combustion of one cubic meter of hydrogen is 2613 Calories. The question is, therefore: “To

what temperature will 2613 Calories raise one cubic meter of water vapor?" The answer is, using the data above,

$$Q (o-t) = 0.34t + 0.00015t^2 = 2613$$

Whence $t = 3191^\circ$

(2) What is the maximum temperature of the hydrogen flame burning in dry air?

The heat evolved is, as before, 2613 Calories, and there is formed also one cubic meter of water vapor, but the products will contain also the nitrogen which accompanied the 0.5 cubic

meter of oxygen necessary for combustion, viz.: $\frac{0.5}{0.208} - 0.5$

= 1.9 cubic meters, and this is heated as well as the water vapor. Therefore,

$$Q (o-t) = (0.34t + 0.00015t^2) + 1.9 (0.303t + 0.000027t^2) = 2613$$

Whence $0.916t + 0.0002013t^2 = 2613$

And $t = 2010^\circ$

(3) What is the temperature of the air-hydrogen blowpipe, if 25 per cent. excess of air is used, above that required?

All the data are the same as above, except that to the products will be added 0.25 (0.5+1.9) = 0.6 cubic meters of unused air, which has the same specific heat as nitrogen, and therefore the equation becomes

$$Q (o-t) = (0.34t + 0.00015t^2) + 2.5 (0.303t + 0.000027t^2) = 2613$$

Whence $t = 1764^\circ$

This calculation brings out very clearly the uselessness and ineffectiveness of using more air than is theoretically necessary; any excess simply passes unused into the products of combustion, and thus reduces their maximum possible temperature. The obtaining of the maximum possible temperature depends upon accurately proportioning the supply of oxygen or air to the quantity of gas burned; an excess or a deficiency will result in a lower temperature.

COMBUSTION WITH HEATED FUEL OR AIR.

If the fuel itself or the air which burns it is preheated, the sensible heat in either one or in both is simply added to the heat generated by the combustion, to give the total amount of

heat which must be present as sensible heat in the products of combustion. The effect is exactly the same as if the heat developed by combustion had been increased by the sensible heat in the fuel or air used.

What is the calorific intensity (theoretical maximum temperature) obtained by burning carbonous oxide gas? (a) Cold, with cold air; (b) cold, with hot air at 700°C .; (c) hot, with hot air, both at 700°C .

(a) Take one cubic meter of carbonous oxide. Calorific power 3,062 Calories; product one cubic meter of carbonic oxide, and 1.904 cubic meters of nitrogen.

Let t be the temperature attained; then

$$\begin{array}{ll} \text{Heat in the} & 1 \text{ m}^3 \text{ carbonic oxide} = 0.37t - 0.00022t^2 \\ \text{" " " " } & 1.904 \text{ m}^3 \text{ nitrogen gas} = 0.577t + 0.0000514t^2 \\ \text{" " " " } & \text{products} = 3,062 \text{ Cal's.} = \frac{0.947t + 0.0002714t^2}{t = 2050^{\circ}} \end{array}$$

Whence

(b) If the 2.404 cubic meters of air needed are preheated to 700°C ., they will bring in as sensible heat

$$\begin{aligned} Q (0-700) &= 2.404 [0.303 (700) + 0.000027 (700)^2] \\ &= 552 \text{ Calories.} \end{aligned}$$

The total heat in the products will be $3062 + 552 = 3614$ Calories, and therefore $0.947t + 0.0002714t^2 = 3614$

Whence

$$t = 2189^{\circ}$$

(c) If the gas itself is also preheated it brings in

$$\begin{aligned} Q (0-700) &= 0.303 (700) + 0.000027 (700)^2 \\ &= 225 \text{ Calories.} \end{aligned}$$

The total heat in the products will be $3614 + 225 = 3839$ Calories, and therefore $0.947t + 0.0002714t^2 = 3839$

Whence

$$t = 2284^{\circ}$$

Heating both gas and air to 700° before they burn thus raises the theoretical temperature from 2050 to 2284 or 234° .

Problem 5.

Statement.—The natural gas of Kokomo, Ind., contains by analysis: Methane (marsh gas) 94.16, ethylene (olefiant gas)

0.30, hydrogen 1.42, carbonous oxide 0.55, carbonic oxide 0.27, oxygen 0.32, nitrogen 2.80, hydrogen sulphide 0.18,—in percentages, by volume.

Required:

(1) The maximum flame temperature, if burned cold with the theoretical amount of cold, dry air necessary.

(2) The calorific intensity, if burned cold, with the requisite air preheated to 1000° C.

(3) The calorific intensity, if burned cold, with 25 per cent. more air than theoretically necessary, preheated to 1000°.

Solution:

[The practical calorific power of this gas has been already calculated in Problem 4 as 8203 Calories per cubic meter. The gas itself is always burned cold, because, if preheated, it decomposes and deposits carbon in the regenerators.]

The products of combustion of the gas, say per cubic meter, must first be found, using the formulæ for combustion.

Requirement (1):

	1 Cubic Meter of Gas.	Oxygen Needed. m ³	Products.			
			CO ²	H ² O	SO ²	N ²
CH ⁴	0.9416	1.8832	0.9416	1.8832
C ² H ⁴	0.0030	0.0090	0.0060	0.0060
H ²	0.0142	0.0071	0.0142
CO	0.0055	0.00275	0.0055
CO ²	0.0027	0.0027
O ²	0.0032	0.0032
N ²	0.0280	0.0280
H ² S	0.0018	0.0027	0.0018	0.0018
		<u>1.90155</u>	<u>0.9558</u>	<u>1.9052</u>	<u>0.0018</u>	<u>0.0280</u>
Air required	9.14			(carrying in N ²) =	<u>7.238</u>	
					Total N ²	7.266

The heat generated will exist as sensible heat in the CO², H²O, SO² and N² of the products. The mean specific heat of SO² per cubic meter is 0.444 at ordinary temperatures; what it is at high temperature has not been determined; we will give it the same index of increase as the analogous gas CO²,

and take for it $Sm (o-t) = 0.444 + 0.00027t$, or $Q (o-t) = 0.444t + 0.00027t^2$.

At the temperature attained by combustion, t , the products will contain the following amounts of heat:

$$N^2 = 7.266 (0.303t + 0.000027t^2)$$

$$H^2O = 1.9052 (0.34t + 0.00015t^2)$$

$$CO^2 = 0.9558 (0.37t + 0.00027t^2)^*$$

$$SO^2 = 0.0018 (0.444t + 0.00027t^2)$$

$$\text{Total} = 3.2044t + 0.00074057t^2 = 8203 \text{ Calories.}$$

From which $t = 1806^\circ$ (1)

Requirement (2):

Heat in 1 m^3 of air at $1000^\circ = 0.303 (1000) + 0.000027 (1000)^2$
 $= 330 \text{ Calories.}$

" 9.14 m^3 " $1000^\circ = 3016$ "

Therefore: $3.2044t + 0.00074057t^2 = 8203 + 3016$

Whence $t = 2288^\circ$

Requirement (3):

Excess air used $= 9.14 \times 0.25 = 2.285 \text{ m}^3$.

Heat in 11.425 m^3 at $1000^\circ = 11.425 \times 330 = 3770 \text{ Calories,}$

The heat capacity of the excess air must be added to the heat in the products at temperature t , viz.:

$$\text{Excess air} = 2.285 (0.303t + 0.000027t^2)$$

making the total heat in the products (adding to previous expression):

$$3.8968t + 0.00080227t^2 = 8203 + 3770$$

Whence $t = 2134^\circ$

THE ELDRED PROCESS OF COMBUSTION.

A means of regulating the temperature of the flame has been proposed by Eldred, and described by Mr. Carlton Ellis in the December, 1904, issue of this journal. The proposition is simply to mix with the air used for combustion a certain

* These and some succeeding problems were worked out using this specific heat. Later the author has adopted a slightly different value for CO^2 , viz., $(0.37 + 0.00022t)$, which he now considers more nearly correct.

proportion of the products of combustion themselves. The principle is easily understood when the requisite calculations of the theoretical flame temperatures are made. When solid fuel is burnt the temperature is often too high locally, and results in burning out grate bars or overheating the brick work of the fire-place, or overheating locally the material which is mixed with the fuel. If the air is diluted with products of combustion the initial theoretical temperature is lowered, and the above evils may be obviated. Using solid fuel, the heat in the fuel before the air actually burns it must be added to the heat generated by combustion to get the actual temperature in the hottest part of the fire.

Examples: (1) What will be the highest temperature in a charcoal fire fed by air, assuming complete combustion without excess of air?

Assuming the charcoal to be pure carbon, and to be heated to the maximum temperature t before it burns (by the combustion of the preceding part), the heat available is:

Heat of combustion of 1 kilo of carbon.....	8100 Cal's.
Sensible heat in the carbon at t°	$0.5t - 120$ "
Total heat available to raise the temperature...	$7980 + 0.5t$ "
Products of combustion... ..CO ² 1.85 m ³	
..N ² 7.04 "	
Heat of product at t°CO ² 1.85 (0.37t + 0.00022t ²)	
N ² 7.04 (0.303t + 0.000027t ²)	
Sum	$2.81t + 0.00060t^2$

therefore $2.81t + 0.00060t^2 = 7980 + 0.5t$

whence $t = 2199^\circ$

(2) What will be the temperature in the same case, if the air used is diluted with an equal volume of the products of combustion?

The heat available is the same as before, $7980 + 0.5t$; but since the mixed air for combustion contains only half as much oxygen per cubic meter, the products will be exactly doubled in amount for a unit weight of carbon burnt, and we therefore have directly

$$2(3.378t + 0.00074t^2) = 7980 + 0.5t$$

whence

$$t = 1026^\circ$$

It is therefore evident that the maximum temperature of the hot gases at their moment of formation is nearly halved by the procedure stated.

(3) Taking the cases cited by Mr. Ellis, where the products contained originally 15 per cent. oxygen and 6 per cent. carbon dioxide, and after mixing the air used with half its volume of the chimney gases, 9 per cent. oxygen and 12 per cent. carbon dioxide (the gas-air mixture entering containing 15 per cent. oxygen and 6 per cent. carbon dioxide), what are the maximum temperatures obtained in the two cases?

Case 1: The heat available is as before; the products of combustion are CO^2 1.85 m^3 , O^2 4.62 m^3 , N^2 24.36 m^3 , and their sensible heat at temperature t —

$$\begin{array}{rcl} \text{Heat in CO}^2 & = & 1.85 (0.37t + 0.00027t^2) \\ \text{“ O}^2 + \text{N}^2 & = & 28.98 (0.303t + 0.000027t^2) \\ \hline \text{Sum} & = & 9.46t + 0.00128t^2 \end{array}$$

therefore $9.46t + 0.001280t^2 = 7980 + 0.5t$

whence $t = 800^\circ$

Case 2: The products, per kilogram of carbon burnt, will be CO^2 3.70 m^3 , O^2 2.77 m^3 , N^2 24.36 m^3 , and we have

$$\begin{array}{rcl} \text{Heat in CO}^2 & = & 3.70 (0.37t + 0.00027t^2) \\ \text{“ O}^2 + \text{N}^2 & = & 27.13 (0.303t + 0.000027t^2) \\ \hline \text{Sum} & = & 9.09t + 0.00173t^2 \end{array}$$

therefore $9.09t + 0.00173t^2 = 7980 + 0.5t$

whence $t = 764^\circ$

Conclusions: The calculations regarding the Eldred process bring out what was not stated in the printed description of the method, viz.: that if a small excess, or no excess of oxygen escapes, to the chimney, the temperature of the flame will be greatly reduced by the dilution of the air used, because more gas-air mixture will be required per unit of fuel burnt; but if there is any large amount of unused oxygen escaping in the first instance, the dilution practiced will scarcely affect the temperature of the flame at all, because it makes very little difference whether the fuel is heating up unused oxygen or carbon dioxide dilutant substituted for some of it, as long

as there is more than enough oxygen to burn the fuel. The fact of the specific heat of carbon dioxide being greater than that of oxygen, is the only reason for the small calculated difference of 36° , in cases 1 and 2. It is true that the dilution practiced will result in less heat being lost in the waste gases, in the *Example* (3), but the same economy could be obtained by simply using less excess of air in the first instance.

TEMPERATURES IN THE "THERMIT" PROCESS.

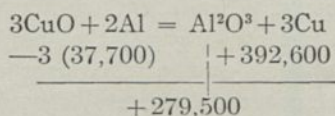
The Goldschmidt process of reducing metallic oxides by powdered aluminium, igniting the cold mixture, is only a special case of our general rule, as far as concerns the calculation of the theoretical temperatures obtained. In any case, the total heat available is the surplus evolved in the chemical reaction, and the temperature sought is that to which this quantity of heat will raise the products of the reduction. The products are alumina and the reduced metal. The heat in the latter, in the melted state, is well known in many cases; it is most clearly expressed by the sum of the heat in such melted metal just at its melting point (which is easily determined calorimetrically, and is well known for many metals), plus the heat in the melted metal from the melting point to its final temperature, which is equal to t , minus the melting temperature, multiplied by the specific heat in the melted condition. These data are known for many metals; for some they may have to be assumed from some general laws correlating these values. The heat in melted alumina has not been determined calorimetrically, to my knowledge. Its sensible heat solid is $0.2081t + 0.0000876t^2$ (determination made in author's laboratory), which, evaluated for the probable melting point, 2200° C., would give the heat in it at that temperature 881.8 Calories; the latent heat of fusion of molecular weight is very probably $2.1 T$, where T is the absolute temperature of the melting point, making the latent heat of fusion per kilogram $2.1 (2200 + 273) \div 102 = 5193 \div 102 = 50.9$ Calories. The specific heat in the melted state is probably equal to the specific heat of the solid at the melting point, viz.: $0.2081 + 0.0001752 (2200) = 0.5935$. We, therefore, have for the heat in melted alumina at temperature t —

Heat in solid alumina to the melting point.....	881.8	Calories
Latent heat of fusion.....	50.9	"
Heat in liquid alumina to its setting point	0.5935	(t-2200)
	Total. 932.7 + 0.5935 (t-2200)	
or, for a molecular weight, 102 kilograms:	95,135	+ 60.54 (t-2200).

Examples:

(1) If black cupric oxide is reduced by powdered aluminium what is the temperature attained?

The reaction is



The products must therefore be raised to such a temperature that they contain 279,500 Calories. The heat in molecular weight of alumina at temperature t has already been found; that in copper at t° is, for one kilogram (using the author's determinations):

Heat in melted copper at setting point = 162 Calories.

Heat in melted copper above $1065^\circ = 0.1318 (t-1065)$ Calories.

Total = $162 + 0.1318 (t-1065)$.

Per atomic weight (63.6 kilos.) = $10303 + 8.3825 (t-1065)$

From these data there follows the equation:

$$\begin{aligned}
 95,135 + 60.54 (t-2200) + 3[10,303 + \\
 8.3825 (t-1065)] = 279,500 \\
 \text{whence} \quad t = 3670^\circ
 \end{aligned}$$

A little further calculating will show that approximately one-third of all the heat generated exists in the copper, and two-thirds in the melted alumina.

(2) If pure ferric oxide is reduced by the "Thermit" process, what is the temperature of the resulting iron and melted alumina?

The reaction and the heat evolved have been already given in the preceding instalment of these calculations (page 30.) They show that per molecular weight of alumina formed there are two atomic weights (112 kilos.) of iron formed, and there is disposable altogether 197,000 Calories. The heat in a kilo-

gram of pure iron at its melting point (1600°) is 300 Calories, the latent heat of fusion approximately 69 Calories, and the specific heat in the melted condition 0.25. The total heat in a kilogram of melted iron is therefore $369 + 0.25 (t - 1600)$ Calories, or per atomic weight = $20,664 + 14 (t - 1600)$ Calories.

We, therefore, can write the equation:

$$95,135 + 60.54 (t - 2200) + 2[20,664 + 14 (t - 1600)] = 197,000$$

whence $t = 2694^\circ$

A similar calculation made for the reduction of MnO by the theoretical amount of aluminium, shows a reduction temperature less than the melting point of alumina. This would mean that the melting down of the mass to a fused slag of pure alumina could not take place. What happens in the reduction of manganese is that an excess of manganous oxide is used, whereby all the aluminium is consumed, and none at all gets into the reduced manganese, and, furthermore, the excess of manganous oxide unites with the alumina to form a slag of manganous aluminate, which is fusible at the temperature attained. Without the latter arrangement no fused slag could result.

Similar calculations, made with silicon as the reducing agent, show similar difficulties regarding the theoretical temperatures attainable, when iron or manganese are reduced. By using an excess of the oxides of these metals, however, calculation shows that temperatures sufficient to fuse the metals and the manganous silicate, or ferrous silicate produced, ought to be obtained.

CHAPTER IV.

THE THERMOCHEMISTRY OF HIGH TEMPERATURES.

The problem is: Knowing the heat evolved (or absorbed) in the formation of a compound, or in a double reaction, starting with the reacting materials cold, and ending with the products cold, what is the heat evolved (or absorbed) in either of the following cases?

(a) Starting with the reagents cold and ending with the products hot.

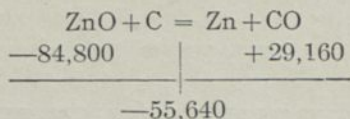
(b) Starting with the reagents hot and ending with the products hot.

(c) Starting with the reagents hot and ending with the products cold.

Of these three cases (b) is the most general form of the problem, and occurs frequently in metallurgical practice, particularly in electrometallurgy; (a) is a more limited form, and requires less data for its calculation, while it is very frequently the desideratum in discussing the thermochemistry or heat requirements of a metallurgical process; (c) is derivable at once if the data exist for calculating (b), and is of such rare occurrence in practice that we can dispense with its lengthy discussion.

The thermochemical data already given and described in preceding sections enable us to calculate the heat of any chemical reaction starting with cold reagents and ending with the products cold. For instance: $(\text{Zn, O}) = 84,800$ Calories means that if we take 65 kilograms of solid zinc, at room temperature, and 16 kilograms of oxygen, as gas at room temperature, ignite them, and after the reaction cool the 81 kilograms of zinc oxide formed down to the same starting temperature, there will be developed a total of 84,800 Calories. Similarly, using the datum $(\text{C, O}) = 29,160$ Calories, we can construct

and interpret the reduction reaction, starting with cold materials and finally ending with cold materials, as follows:



This reaction, as interpreted, stands for none of the above cases (*a*), (*b*) or (*c*); in fact, it represents only a calorimetric determination in the laboratory, and does not correspond to either of the three cases actually taking place in practice, that is, it is not directly applicable to practical conditions, without being modified by the conditions actually arising in practice.

Case (a): If we, in practice, start with the reagents cold, and the products pass away from the furnace hot, at some determined temperature *t*, the total heat energy necessary to cause this transformation is calculable in two ways. The first way is to follow the course of the reaction, and to say that the total heat absorbed is that necessary to heat the reacting bodies to the temperature *t*, plus the heat of the chemical reaction assumed as starting and finishing at that temperature. The first of these items can be obtained if we know the sensible heat in the reacting bodies up to the temperature *t*; it is a question of specific heats of the reacting bodies up to *t* (including any physical changes of state occurring in them between 0 and *t*); the second item requires a knowledge of the heat of formation of all the compounds involved, starting with their ingredients at *t*, and ending with the products at *t*. But the latter item is the general question of the heat of a reaction starting with the ingredients hot and ending with the products hot; it is the most general case, which we have designated as *Case (b)*, and which will be discussed later. This way of solving *Case (a)*, therefore, really includes the solution of *Case (b)*, and we will defer its consideration for the present. The second method of solving *Case (a)*, and one which does not involve the more general solution, is to take the heat of the reaction, starting with the ingredients cold and ending with the products cold—the ordinary heat of the reaction from ordinary thermochemical data—and to add to this

the amount of heat which would be required to raise the products from zero to the temperature t . This, of course, does not actually represent the sequence in which the reactions take place in practice, but it accurately represents the heat involved or evolved in passing from the cold reagents to the hot products, and is, therefore, exactly the practical quantity which we are endeavoring to find. Moreover, it involves a knowledge of only the specific heats of the products, and not that of the ingredients or substances reacting.

Illustration: Starting with a mixture of zinc oxide and carbon in the proportions Zn O and C, at ordinary temperature, and shoveling them cold into a retort, how much heat is absorbed in converting them into Zn vapor and CO gas, issuing from the retort at 1300° C.?

If we start to calculate this quantity, by first finding the heat necessary to heat Zn O and C up to 1300° , that is obtained by multiplying the weights of each by their mean specific heats from 0° to 1300° , and then by 1300, as follows:

	Calories.
81 kilos. ZnO \times $[0.1212 (1300) + 0.0000315 (1300)^2]$	= 17,075
12 " C \times $[0.5 (1300) - 120]$	= 6,360
	Sum = 23,435

To this must then be added the heat of the reaction $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$, starting with the reacting bodies at 1300° , and ending with the products at the same temperature. This can only be found by solving the general *Case (b)* for this particular reaction, which we will find involves a knowledge of the heat required to raise Zn, O, C, ZnO and CO from 0° to t . Anticipating such a solution, we may say that the heat of the reaction starting and ending at 1300° is—80,160 Calories, making the sum total of energy required 103,601 Calories.

The solution is usually much simpler if we take the second method, and add to the heat of the reaction, starting and ending at zero (—55,640 Calories), the heat required to raise 65 kilos. of zinc and 28 kilos, (22.22 cubic meters) of carbonous

* Heat in 1 kilo of carbon, for temperature above $1,000^{\circ}$, $0.5 t - 120$ (deduction from Weber's results); zinc oxide $0.1212 t + 0.0000315 t^2$ (determination by the author).

oxide, from their ordinary condition at zero to their normal condition at 1300°. The calculation for the CO gas is simply:

$$2.22 \times [0.303 (1300) + 0.000027 (1300)^2] = 9,766 \text{ Calories.}$$

For the zinc, the calculation is more complicated:

Heat in solid zinc to the melting point

(420°):

$$65 \times [0.09058 (420) + 0.000044 (420)^2] = 2,977 \text{ Calories.}$$

Latent heat of fusion $65 \times 22.61 = 1,470$ "

Heat in melted zinc, 420° to boiling point

(930°):

$$65 \times [0.0958 + 0.000088 (420)] \times (930 - 420) = 4,228$$
 "

Latent heat of vaporization (Trouton's rule)

$$20 \times (930 + 273) = 27,670$$
 "

Heat in zinc vapor (monatomic) $5 \times (1300$

$$- 930) = 1,850 \text{ Calories.}$$

$$\text{Sum} = 38,195$$
 "

The total sensible heat required is, therefore, $9,766 + 38,195 = 47,961$ Calories, which, added to the 55,640 absorbed in the chemical reaction, if it started and ended at zero, makes a total heat requirement of 103,601 Calories for the practical carrying out of this reaction, starting with the reagents cold and ending with the hot products at 1300°.

[To be absolutely accurate, regard should be paid in the above case to the fact that the above calculations are based on the substances being all at atmospheric pressure, while in the mixture of Zn vapor and CO gas each is under only 0.5 atmospheric tension. Since each of these represents a molecular weight, the outer work which has been included in the calculations is $2 \times 2T = 2 \times 2 (1300 + 273) = 6292$ Calories, whereas it should really be only half that much, or 3146 Calories. The corrected heat required is, therefore, $103,601 - 3,146 = 100,455$ Calories, or 1,545 Calories per kilogram of zinc. This datum is exactly the net heat requirement on which calculations of the net electrical energy required to produce zinc from its oxide, or calculations of the net efficiency of an ordinary zinc furnace, would be based.]

Case (b): To calculate the heat of a chemical reaction starting and finishing at any temperature t , two methods are available; The most general solution, and that easiest to understand, is to calculate for each compound involved the heat of its formation at the temperature t , that is, the heat evolved if the elements start at t and the product is cooled to t . Having these heats of formation at t , they are used in the equation in just the same manner as the heats of formation at zero are ordinarily used in obtaining the heat of the reaction starting and ending at zero. The calculations are based on this general principle: The heat evolved when the cold elements unite to form the hot product at temperature t equals the heat of union at zero, minus the heat necessary to raise the product from zero to t ; if to this difference we add the heat which would be necessary to heat the uncombined elements from zero to t , the sum is the desired heat of formation at t° .

Illustration: The heat of formation of ZnO at zero is 84,800, starting with cold Zn and O and ending with cold ZnO. If we started with cold Zn and O and ended with hot ZnO, say at 1300° , the heat evolved altogether would be less than 84,800 by the sensible heat in the 81 kilograms of ZnO at 1300° , which has already been calculated (see previous illustration) to be 17,075 Calories. The difference is 67,725 Calories, and represents the transformation from cold Zn and O to hot ZnO. If the Zn and O were heated to 1300° before combining, they would contain as sensible heat the following quantities:

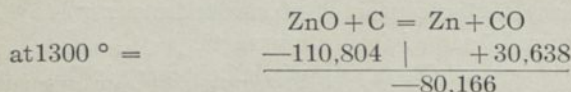
Heat in 65 kilograms of Zn (0 to 1300°)	
	already calculated 38,195 Calories
Heat in 16 kilograms of O = $11.11 \text{ m}^3 \times$	
	$[0.303 (1300) + 0.000027 (1300)^2] = 4,884$ “
	Sum <u>43,079</u> “

And the heat evolved in passing from the hot reagents to the hot product at 1300° must be 67,725 plus this sensible heat, or 110,804 Calories. We can express this datum as follows: $(\text{Zn, O})^{1300} = 110,804$, which means that when the zinc and oxygen taken in their normal state at 1300° combine to form ZnO at 1300° , 110,804 Calories are evolved.

A similar calculation for CO is as follows:

	(C, O) = 29,160 Calories
Sensible heat in CO (0 to 1300°) already calculated =	9,766 "
Heat evolved when cold C and O form CO at 1300° =	19,394 "
Sensible heat in C (0 to 1300°) =	6360
" " O (") =	4884 11,244 Calories
Heat evolved hot C and O to hot CO =	Sum = 30,638 "
Or	(C, O) ¹³⁰⁰ = 30,638 "

Uniting the two data found, for the heats of formation of ZnO and CO at 1300°, in the equation of reduction, we have



The actual reduction is thus seen to absorb 24,526 Calories more at 1300° than at zero, an increase of over 42 per cent.

If to this heat of reaction at 1300° we add the heat necessary to raise the ZnO and C to 1300° (already calculated under *Case (a)* as 23,435 Calories), we will have a total heat requirement of 103,601 Calories, which would be required practically if we started with cold ZnO and C and ended with the hot Zn and CO. This agrees, as it indeed must, with the sum of the heat absorbed in the reaction at zero, 55,640, increased by the sensible heat in Zn and CO at 1300°, already found to be 47,691, or a total of 103,601.

Another method of calculating the heat of the reaction $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$ at 1300°, without using the heat of formation of ZnO and CO at 1300°, is based on the following general principle: If from the heat of any reaction, starting and ending cold, there be subtracted the heat necessary to raise the products from 0 to t , the difference is the heat of the transformation from cold reagents to hot products; if to this be added the heat which would be contained in the reagents if they were heated to t , the sum is the heat of transformation from heated reagents to heated products, all at the temperature.

Illustration: The heat of the reaction we have been studying, starting and ending cold, is —55,640 Calories

Sensible heat in Zn at 1300°	= 38,195			
" " CO "	= 9,766	47,691	"	
		Difference—	103,601	"
Sensible heat in ZnO at 1300°	= 17,075			
" " C "	= 6,360	23,435	"	
		Sum—	80,166	"

The above is the simplest way of calculating the heat of any chemical reaction at any desired temperature, since it involves the knowledge of the heat capacities of only those substances which occur individually in the reaction, and not that of the elements of which the compounds present are composed. The above calculation, for instance, involves the heat capacities of ZnO, C, Zn, and CO, but not that of oxygen, which does not occur free in the reaction.

Case (c): This hardly needs discussion, because if we have the data for calculating *Case (b)*, this case can be easily worked. If to the heat of the reaction at t° we add the heat given out by the products in cooling from t to 0, the sum is the total heat evolved in passing from the hot reagents to the cold products. This solution of the problem presupposes, however, the solution of *Case (b)* and requires the maximum amount of data, but it has the advantage of following and representing the logical course of the reaction. A simpler solution is to add to the heat of the cold reaction at zero, the heat necessary to heat the ingredients to t , and the sum will be the quantity required.

Illustration: Taking the same case as before:

Heat of reaction at 1300°	= —80,166			
Sensible heat in products at 1300°	= 47,961			
		Sum =	—32,205	
or, Sensible heat in reagents at 1300°	= 23,435			
Heat of reaction at zero	= —55,640			
		Sum =	—32,205	

The reasoning involved in the above is simply that, starting with the reagents hot and ending with the products cold, the

heat evolution must be the same whether we suppose the system to pass along the one path or the other.

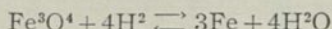
GENERAL REMARKS.

It will be evident from this enunciation of principles and the illustrations adduced, that for many practical purposes the calculation according to *Case (a)* will suffice for finding the net energy involved in many metallurgical operations; it gives the sum total of energy necessary to be supplied to pass from the cold reagents to the hot products as they come from the furnace, but the two items of which this sum is composed do not actually represent the two items of the division of this total in the furnace, *i.e.*, into heat necessary to heat the reagents to the reacting temperature and heat actually absorbed as the reaction takes place. The latter item can only be calculated by one of the two methods explained under *Case (b)*, and then the former item can be obtained by difference, or by direct use of the heat capacities of the reacting substances.

It is, of course, obvious that this whole subject of calculating the thermochemistry of high temperatures (as distinguished from the ordinary *zero thermochemistry*) necessitates the use of all available data regarding specific heats in the solid, liquid and gaseous states of both elements and compounds, and also in many cases of their latent heats of fusion and vaporization. When, however, the necessary physical data are known, or can be assumed with approximate accuracy, the way is open to make many calculations of the greatest value in practical metallurgy and chemistry. The exact heats of formation of chemical compounds at a certain temperature, which may be, and often are, very different from these values at zero, and, having frequently different relations to each other, will explain in many cases many hitherto little understood and apparently contradictory reactions. The calculations also enable us to understand many reactions taking place only at high temperatures, to calculate whether they are really exothermic or endothermic at the temperatures at which they occur, and to compare these data with the data as to the heat of such reactions obtained by studying the chemical equilibrium of such reactions and deducing the heat of the reaction from the rate of displacement of the chemical equilibrium. One such ex-

ample may suffice to suggest the large field here open to the scientific metallurgist.

Example: G. Preuner (*Zeitschrift für Physikalische Chemie*, March 15, 1904, p. 385) reports a long and careful investigation of the equilibrium of the reaction



in which he finds the equilibrium constant for different temperatures, and calculates from its value at 960°, by the use of Van't Hoff's formula, that the heat value of the reduction at that temperature is—11,900 Calories, and noticing the great difference between this value and the value derived from the ordinary heats of formation ($-270,800 + 4(58,060) = -38,560$), he concludes that the Van't Hoff formula gives wrong results when applied to this class of reactions. Now, the facts are that Preuner's observations were good, Van't Hoff's formula is correct, and applies, but the thermochemical value of the reaction,—38,560 Calories is the correct value only for *the reaction beginning and ending at ordinary temperature*. Our thermochemical principles enable us to calculate the heat of the reaction at 960°, as follows:

Heat of the reaction beginning and ending at
zero = — 38,560 Calories

Heat in products at 960°:

$$3\text{Fe} = 3(56) \times [0.218(960) - 39] \text{ Pionchon} = 28,560$$

$$4\text{H}^2\text{O} = 4(22.22) \times [0.34(960) + 0.00015(960)^2] = \underline{41,300} \quad 69,860 \text{ Calories}$$

Heat in reagents at 960°:

$$\text{Fe}^3\text{O}^4 = 232 \times [0.1447(960) + 0.0001878(960)^2]^* = 72,384$$

$$4\text{H}^2 = 4(22.22) \times [0.303(960) + 0.000027(960)^2] = \underline{28,075} \quad 100,459 \quad "$$

The heat of the reaction at 960° is, therefore, according to our method of *Case (b)*, $-38,560 - 69,860 + 100,459 = -7,961$

* Approximate determination of heat in Fe^3O^4 , made recently in author's laboratory, $Q = 0.1447t + 0.0001878t^2$.

Calories. It thus appears that Preuner's dilemma was mostly caused by his thinking that the thermochemical value of the reaction at zero should be a constant for any temperature: a proper thermochemical calculation removes the dilemma.

Since the whole treatment of the subject of the thermochemistry of high temperatures requires a knowledge of data concerning the heat capacity of elements and compounds in the solid, liquid and gaseous states, as well as of their latent heats of fusion and vaporization, the next instalment of these calculations will supply these data as far as they are known, and discuss a number of applications of these principles to various metallurgical processes.

In order to apply the principles explained in the preceding discussion, two sets of data are necessary; first, the thermochemical data, such as are ordinarily obtained by laboratory experiments at laboratory temperatures; second, physical data concerning the specific heats and latent heats of fusion, and volatilization of elements and compounds. The first have been given, at least for all important compounds met with in metallurgy, in a previous paper (April), the latter will now be discussed and the data presented as far as they have been determined.

SPECIFIC HEATS OF THE ELEMENTS.

Dulong and Petit's law announces the fact that the specific heat of atomic weight of a solid metal is nearly constant, the value varying between 6 and 7, and averaging 6.4. This generalization was made chiefly upon the basis of the specific heats of the metals, as determined in the range 100° C. to 10° or 15° C., such as in Regnault's accurate experiments. About the only notable exceptions to this rule are carbon, boron and silicon, and it has been naively remarked by more modern physicists that these exceptions to the rule disappear if we find the specific heat of these three elements at high temperatures, that, for instance, the specific heat of carbon above 1000° C. is 0.5, making its atomic specific heat $0.5 \times 12 = 6$, and therefore the exceptions to the rule are all accounted for. Now, the rule is an important one, and has done good service, but the exceptions just noted and their behavior at high temperatures really prove that the rule must be made more general, or else

abandoned altogether. The fact is, that the specific heats of almost all the solid elements increase with the temperature at a rate equal to an increase of about 0.04 per cent. of their value for each degree centigrade, so that the atomic specific heat of the majority of the elements, which is about 6.4 at ordinary temperatures, becomes about 40 per cent. greater at 1000° C. for such elements as are not melted at that temperature. Therefore, while we may say that at ordinary temperatures the specific heat of atomic weight of a solid element is 6.4, and its specific heat per unit of weight is 6.4, divided by the atomic weight, yet it will be more accurate, if actual determinations have not been made, to assume that the actual specific heat increases 0.04 per cent. for every degree rise in temperature, and mean specific heat to zero half that fast.

The specific heat in the liquid state has not been determined for many elements. It is in general higher than the specific heat of the solid at ordinary temperatures; in fact, it appears to be more nearly equal to the specific heat of the solid element just before fusion, and may be so assumed if no determinations have been made. It is found, furthermore, not to change perceptibly with rise of temperature, so that it may be assumed constant.

The specific heat of the gaseous elements has been determined only for those which are gaseous at low temperatures. For the metals which, as far as known, have monatomic vapors, *i.e.*, vapors in which the atoms exist alone and uncoupled with each other, the specific heat of atomic weight, occupying 22.22 cubic meters at standard conditions, should be theoretically 5.0 Calories at constant pressure, or 0.225 per cubic meter. We may thus estimate the specific heat of metallic vapors which have not been determined.

LATENT HEATS OF FUSION OF THE ELEMENTS.

The passage from the solid to the liquid state is in all cases accompanied by an absorption of heat, which in amount varies from one or two Calories up to 100 Calories per unit of weight. This quantity has been most frequently determined by finding calorimetrically how much heat is given out by unit weight of the melted element just at its setting point, in cooling to

ordinary temperatures, and subtracting from this the heat in unit weight of the solid substance at the melting point, as determined most accurately by extrapolating the value of mean specific heat of the solid up to the melting point. In this manner the latent heat of fusion for a number of elements has been directly determined.

If a crucible full of melted metal is allowed to cool, the temperature falls regularly until the melting point is reached, and then stays constant, or nearly so, for some time, while the metal is setting. A comparison of the rate of cooling before and after setting, with the length of time during which the temperature was constant, gives the relative value of the latent heat of fusion in terms of the specific heat of the melted metal and of the solid metal near to the melting point.

While the latent heat of fusion per unit weight shows no perceptible regularities, it is found that as soon as the latent heat of fusion is expressed per atomic weight of the element (analogous to specific heat of atomic weight) that notable regularities appear. The elements with high melting points have high atomic heats of fusion, and *vice versa*, so that if the elements are arranged in the order of their melting points their latent heats of fusion per atomic weight of each are in the same order, and very nearly proportionately so. If, for instance, a chart or diagram is made, using the melting points as abscissas, and latent heats of fusion of atomic weights as ordinates, the latter will lie very nearly in a straight line. Numerically, if the melting points be expressed in degrees of absolute temperature (centigrade temperatures plus 273), the latent heats of fusion of atomic weights average about 2.1 times the temperature of the melting point. This rule may be used to predict an undetermined latent heat of fusion.

In addition to the above general rule, another one bearing on the same question was also discovered and applied by the writer. (See *Journal of the Franklin Institute*, May, 1897.) According to this observation, the continued product of the latent heat of fusion of atomic weight and the coefficient of expansion and the cube root of the atomic volume (atomic weight divided by specific gravity) is a constant. If the coefficient of linear expansion between 0° and 100° C. is used,

the constant is 0.095, or if the actual linear expansion of unit length from 0° to 100° C. is used, the constant is 9.5. This rule, applied to all elements whose latent heat of fusion is known, gives satisfactory agreements, and enables us therefore to predict the latent heat of fusion of nearly a dozen other elements for which the coefficient of expansion is known.

LATENT HEATS OF VAPORIZATION OF THE ELEMENTS.

This datum has been determined for but a very few elements. Some of the metalloids, like sulphur, phosphorous and arsenic, are known to become complex vapors immediately above their boiling point, corresponding to such formulæ as S^8 , P^4 , As^4 ; the metals, as far as they have been tested, pass into monatomic vapors, such as Na, K, Hg, Zn and Cd, in which each atom represents a molecule. In the latter cases the following generalization may be made: The latent heat of vaporization of atomic weight is proportional to the absolute temperatures of the boiling point at atmospheric pressure, and is numerically equal to about twenty-three times that temperature (twenty-one times, if the outer work of overcoming the atmospheric pressure be not included). From this rule it is possible to estimate the amount of heat necessary to vaporize any metal whose boiling point under atmospheric pressure is known.

Examples: The boiling point of carbon under atmospheric pressure is 3,700° C., and if its vapor is monatomic, the latent heat of vaporization is, for an atomic weight of carbon ($C = 12$), $23 \times (3700 + 273) = 92,080$ Calories, equal to 7,673 Calories per kilogram of carbon. If the vapor is diatomic, and its formula C^2 , then the above latent heat is for twenty-four parts of carbon, and for one part by weight is 3,837 Calories. Other considerations, from thermochemistry, make the latter value the more probable one.

The boiling point of cadmium is 772° C., and its vapor is known to be monatomic, what is its latent heat of vaporization? The atomic weight being 112, the latent heat of vaporization of this quantity is $23 \times (772 + 273) = 24,035$ Calories, which is 215 Calories per kilogram.

In making such calculations it must be strictly observed that the boiling point *under atmospheric pressure* is to be used, and not any temperature at which vapors may appear at partial

tensions which may be only small fractions of atmospheric pressure.

THEMOPHYSICS OF THE ELEMENTS.

Having laid down the laws and the empirical rules which appear to govern these phenomena, we will now discuss the data for the common elements, giving both what is known and what may be assumed as probably true wherever actual determinations have not been made. The elements will be taken up in the order of their atomic weights,—the only scientifically logical order.

In all cases, the actually measured *mean* specific heats, S_m , will be given. In the case of gases, these will be the mean specific heats under constant pressure; if they are desired under constant volume the amount of outer work must be calculated in Calories (two Calories per degree for a molecular weight of a gas, 0.09 Calories per degree for 1 cubic meter, and $0.09 \div$ weight of 1 cubic meter for a kilogram of gas), and subtracted from the specific heat at constant pressure. The specific heat of 1 cubic foot is, in pound Calories, the specific heat per cubic meter divided by 35.32 and multiplied by 2.204, or, in brief, multiplied by 0.0624; in British thermal units it will be the same as in pound Calories, since t is then Fahrenheit degrees.

If, from the data given, it is desired to find the mean specific heat between any two temperatures, t and t' , instead of the mean specific heat from t to 0° , as given directly by the formula, it need only be observed that S_m from t' to t is obtainable by finding S_m from 0° to $(t'+t)$. If, for instance, S_m (0 to t) = $0.303 + 0.000027t$, then S_m (t to t') = $0.303 + 0.000027(t'+t)$. Furthermore, if the actual specific heat at any temperature t is desired, it is equal to the mean specific heat from 0° to $2t$; *e.g.*, in the above cases, S (at any temperature t) = $0.303 + 0.000027(2t)$ = $0.303 + 0.000054(t)$.

Temperatures will be always given and represented in centigrade degrees, except where the specific heat is given in British thermal units, in which case t represents, of course, Fahrenheit degrees, and will also be printed in italics, t , to further distinguish it from t in centigrade degrees. Absolute temperatures, if used, will be designated as T , and are equal to $t + 273$.

HYDROGEN.

From the experiments of Mallard and LeChatelier we deduce:

Sm (0—t) 1 kilogram (up to 2000° C.) =	3.370 + 0.0003t Calories.
1 pound (up to 2000° C) =	3.370 + 0.0003t pound Calories.
1 pound (up to 3600° F.) =	3.370 + 0.00017t B. T. U.
1 cu. meter (up to 2000° C.) =	0.303 + 0.000027t Calories.
1 cu. foot (up to 2000° C.) =	0.0189 + 0.0000017t pound Calories.
1 cu. foot (up to 3600° F.) =	0.0189 + 0.0000009t B. T. U.

For higher temperatures, such as electric furnace heats between 2000° and 4000° C. (3600° to 7200° F.), Berthelot and Vielle have made experiments which give us:

Sm (0—t) 1 kilogram	= 2.75 + 0.0008t Calories.
1 pound	= 2.75 + 0.0008t pound Cal.
1 pound	= 2.75 + 0.00044t B. T. U.
1 cubic meter	= 0.2575 + 0.000072t Calories.
1 cubic foot	= 0.0161 + 0.0000045t pound Cal.
1 cubic foot	= 0.0161 + 0.0000025t B. T. U.

LITHIUM.

Sm (26° to 100°) (solid)	= 0.9408 (Regnault).
Melting point	= 180° C.
Latent heat of fusion (1 kilo.)	= 73 (calculated).
S (liquid)	= 0.975 (calculated).
Boiling point	= 500° (estimated).
Latent heat of vaporization	= 2.540 Cal. (calculated).
S (gas) pet kilo.	= 0.714 (calculated).
per cubic meter	= 0.225 (assumed).

BERYLLIUM.

Sm (solid)	= 0.3756 + 0.00106t (Humpidge).
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BORON.

Sm (solid)	= 0.22 + 0.00035t (Weber).
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CARBON.

$$\begin{aligned} \text{Sm (amorphous) } t \text{ under } 250^\circ &= 0.1567 + 0.00036t. \\ (250^\circ \text{ to } 1000^\circ) &= 0.2142 + 0.000166t. \end{aligned}$$

$$(\text{for } t \text{ over } 1000^\circ) = 0.5 - \frac{120}{t}$$

Sm (graphite)	= Approximately the same.
Boiling point	= 3700° C.
Latent heat of vaporization	= $23 T = 92,080 \text{ Cal. per molecule.}$ = $3,837 \text{ Cal. per kilo. if vapor is } \text{C}^2.$ = $6,906 \text{ B. T. U. per pound.}$
S (vapor) per cubic meter	= $0.27 \text{ if diatomic (assumed).}$
per kilogram	= $0.25 \text{ if diatomic.}$

NITROGEN.

Sm (0—t) 1 kilogram (up to 2000° C.)	= $0.2405 + 0.0000214t \text{ Cal.}$
1 pound (up to 2000° C.)	= $0.2405 + 0.0000214t \text{ pound Cal.}$
1 pound (up to 3600° F.)	= $0.2405 + 0.0000119t \text{ B. T. U.}$
1 cu. meter (up to 2000° C.)	= $0.303 + 0.000027t \text{ Cal.}$
1 cu. foot (up to 2000° C.)	= $0.0189 + 0.0000017t \text{ pound Cal.}$
1 cu. foot (up to 3600° F.)	= $0.0189 + 0.0000009t \text{ B. T. U.}$

For temperatures between 2000° and 4000° C. the following are the values of the mean specific heats to zero:

Sm (0—t) 1 kilogram	= $0.2044 + 0.000057t \text{ Cal.}$
1 pound	= $0.2044 + 0.000057t \text{ pound Cal.}$
1 pound	= $0.2044 + 0.000032t \text{ B. T. U.}$
1 cubic meter	= $0.2575 + 0.000072t \text{ Cal.}$
1 cubic foot	= $0.1601 + 0.0000045t \text{ pound Cal.}$
1 cubic foot	= $0.0161 + 0.0000025t \text{ B. T. U.}$

OXYGEN.

Sm (0—t)	1 kilogram (up to 2000° C.)	=	0.2104+0.0000187t Cal.
	1 pound (up to 2000° C.)	=	0.2104+0.0000187t pound Cal.
	1 pound (up to 3600° F.)	=	0.2104+0.0000104t B. T. U.
	1 cu. meter (up to 2000° C.)	=	0.303+0.000027t Cal.
	1 cu. foot (up to 2000° C.)	=	0.0189+0.0000017t pound Cal.
	1 cu. foot (up to 3600° F.)	=	0.0189+0.0000009t B. T. U.
Sm (0—t)	1 cu. meter (2000°—4000° C.)	=	0.2575+0.000072t Cal.
	1 cu. foot (2000°—4000° C.)	=	0.0161+0.0000045t pound Cal.
	1 cu. foot (3600°—7200° F.)	=	0.0161+0.0000025t B. T. U.
	1 kilogram (2000°—4000° C.)	=	0.1788+0.00005t Cal.
	1 pound (2000°—4000° C.)	=	0.1788+0.00005t pound Cal.
	1 pound (3600°—7200° F.)	=	0.1788+0.00003t B. T. U.

SODIUM.

Sm (solid) (—38 to +10° C.)	=	0.293 (Regnault).
(0° = t°) (solid)	=	0.2932+0.00019t (Bernini).
Melting point	=	96.5° C.
Latent heat of fusion	=	31.7 Cal. (Johannis).
	=	730 Cal. per atomic weight.
S. liquid (98°—100°)	=	0.333 (Bernini).
Boiling point	=	742° C.
Latent heat of vaporization	=	23T = 23,345 Cal. per Na.
	=	1,015 Cal. per kilogram.
S of vapor per kilogram	=	0.2174 Cal. (calculated).
per pound	=	0.2174 pound Cal.
per pound	=	0.2174 B. T. U.
per cubic meter	=	0.225 Cal.
per cubic foot	=	0.014 pound Cal.
per cubic foot	=	0.014 B. T. U.

MAGNESIUM.

Sm (solid) (22°—98°)	= 0.25 (Regnault).
Melting point	= 750° C. (approximate).
Latent heat of fusion	= 58 Cal. (calculated).
Boiling point	= 1100° (Ditte).
Latent heat of vaporization	= 31,580 Cal. for Mg = 24 (calculated)
	= 1,315 Cal. per kilogram.
S (vapor) per cubic meter	= 0.225 Cal. (assumed for Mg.).
per cubic foot	= 0.014 pound Cal.
per cubic foot	= 0.014 B. T. U.
per kilogram	= 0.2084 Cal.
per pound	= 0.2084 pound Cal.
per pound	= 0.2084 B. T. U.

ALUMINIUM.

Sm (0—t) solid	= 0.2220 + 0.00005t (Richards).
Melting point	= 625°.
Heat in solid at 625°	= 158.3 Cal. (Richards).
Heat in liquid at 625°	= 258.3 Cal. (Richards).
Latent heat of fusion	= 100.0 Cal. (Richards).
S in liquid state	= 0.308 (constant up to 800°) (Pionchon).
Boiling point (estimated)	= 2300° C.
Latent heat of vaporization	= 61,480 Cal. for Al. = 27 (calculated).
	= 2,277 Cal. per kilogram.
S (vapor) per cubic meter	= 0.225 Cal.
per kilogram	= 0.1852 Cal.
per pound	= 0.1852 B. T. U.

SILICON.

Sm (0—t) (solid), up to 234° C.)	= 0.17 + 0.00009t (Weber).
Melting point	= 1430° C. (Elihu Thompson)
Latent heat of fusion	= 3,576 Cal. for Si = 28 (calculated).
	= 127.7 Cal. per kilogram.
Boiling point	= 2800° C. (estimated).

Latent heat of vaporization	= 70,680 Cal. for Si. = 28
	(calculated).
	= 2,524 Cal. per kilogram if vapor is Si
	= 1,262 Cal. if vapor is Si ²
S (vapor) per cubic meter	= 0.225 Cal. (assumed for Si.).
per cubic meter	= 0.205 Cal. (if vapor is Si ²).
per kilogram	= 0.107 Cal. (if vapor is Si ²).

PHOSPHOROUS.

Sm (solid) (—20 to +7°)	= 0.1788.
Melting point	= 44°
Latent heat of fusion	= 156 Cal. for P = 31.
	= 5.03 Cal. per kilogram.
S (liquid) (44° to 51°)	= 0.2045.
Boiling point	= 287°
Latent heat of vaporization	= 23T = 12,880 Cal. per molecule = P ⁴ .
	= 104 Cal. per kilogram.
S (vapor) estimated	= 0.36 Cal. per cubic meter.
	= 0.064 Cal. per kilogram.
	= 0.064 B. T. U. per pound.

SULPHUR.

Sm (solid) (15° to 97°)	= 0.1844 (Regnault).
Melting point	= 114° C.
Latent heat of fusion	= 9.37 Cal. (Person).
S (liquid) (119° to 147°)	= 0.2346 (Person).
Boiling point	= 444.5°.
Latent heat of vaporization	= 72 Cal. per kilogram.
	= 13,825 Cal. for S ⁶ = 192
	= 130 B. T. U. per pound.
S (of vapor) per cubic meter	= 0.50 for S ⁶ up to 500°.
per cubic meter	= 0.315 for S ² above 800°.

CHLORINE.

Sm (constant pressure)	
1 kilogram	= 0.1241 (from 13° to 202°)
	(Regnault).
1 cubic meter	= 0.40 Cal. (from 13° to 202°).
1 cubic foot	= 0.025 pound Cal.
1 cubic foot	= 0.025 B. T. U.

POTASSIUM.

Sm (solid)—78° to +23°	= 0.1602 (Schuz).
(solid) (0°-t)	= 0.1858 + 0.00008t (Bernini).
Melting point	= 58°.
Latent heat of fusion	= 15.7 Cal. (Johannis). = 612 Cal. for K = 39.
Sm (liquid) 98° to 58°	= 0.25 (Johannis). * = 0.2137 (Bernini).
Boiling point	= 730° (Carnelley and Williams).
Latent heat of vaporization	= 23T = 23,069 Cal. for K = 39. = 592 Cal. per kilogram (calculated). = 1065 B. T. U. per pound.
S (vapor) per cubic meter	= 0.225 Cal. (assumed).
per cubic foot	= 0.014 pound Cal.
per cubic foot	= 0.014 B. T. U.
per kilogram	= 0.128 Cal.
per pound	= 0.128 B. T. U.

CALCIUM.

Sm (solid) 0° to 100°	= 0.1704 (Bunsen).
Melting point	= 780°.
Latent heat of fusion	= 2.1T = 2,106 Cal. for Ca. = 40. = 52.6 Cal. per kilogram.

TITANIUM.

Sm (solid) 0° to 400°	= 0.0978 + 0.000147t (Nilson and Pettersson).
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VANADIUM.

Sm (0° to 100°)	= 6.4 for V = 51 (assumed). = 0.125 Cal. per kilogram.
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CHROMIUM.

Sm (15°—60°)	= 0.100 (Kopp) (uncertain).
(0°-t°) (to 600°)	= 0.1039 + 0.00000008t ² (Adler).

MANGANESE.

Sm (14° to 97°)	= 0.1217 (Regnault) (uncertain).
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IRON.

Pinchon's determinations on the soft iron of "Berry" are the best.

$$\text{Sm (0 to } t) \text{ (for } t \text{ up to } 660^\circ) = 0.11012 + 0.000025t + 0.0000000547t^2.$$

Latent heat of change of state = 5.3 Cal, absorbed between 660° and 720° .

$$\text{Sm (0 to } t) \text{ (for } t = 720^\circ \text{ to } 1000^\circ) = 0.218 - \frac{39}{t}$$

Latent heat of change of state = 6.0 Cal. absorbed between 1000° and 1050°

$$\text{Sm (0 to } t) \text{ (for } t = 1050^\circ \text{ to } 1160^\circ) = 0.19887 - \frac{23.44}{t}$$

Melting point = 1600° (Roberts-Austen).

Latent heat of fusion = 70 Cals. (calculated from 2.1 T rule.)
= 69 Cal. (calculated from second rule.)

Heat in solid iron at M. P. = 300 Cal. (calculated).

Heat in liquid iron at M. P. = 370 Cal. (calculated).

S (liquid) estimated* = 0.22.

NICKEL.

Pionchon obtained the following results:

$$\text{Sm (0 to } t) \text{ (for } t \text{ up to } 230^\circ) = 0.10836 + 0.00002233t.$$

Latent heat of change of state = 4.64 Cal. absorbed between 230° and 400° .

$$\text{Sm (0 to } t) \text{ (for } t = 440^\circ \text{ to } 1050^\circ) = 0.099 + 0.00003375t + \frac{6.55}{t}$$

Melting point = 1450° .

Latent heat of fusion = 62 Cal. by 2.1 T rule.
= 68 Cal. by second rule.

COBALT.

$$\text{Sm (0 to } t) \text{ (for } t \text{ up to } 900^\circ) = 0.10584 + 0.00002287t + 0.000000022t^2 \text{ (Pionchon).}$$

$$\text{Sm (0 to } t) \text{ (for } t \text{ over } 900^\circ) = 0.124 + 0.00004t - \frac{14.8}{t} \text{ "}$$

Latent heat of fusion = 68 Cal. (calculated).

* See Appendix, p. 201, for some more recent data.

COPPER.

Sm (0 to t)	= 0.0939 + 0.00001778t (Frazier and Richards).
Melting point	= 1085°.
Heat in melted copper at M. P.	= 162 Cal. (Frazier and Richards).
Latent heat of fusion	= 43.3 Cal. (observed) Frazier and Richards).
	= 44.8 Cal. (calculated by 2.1 T rule).
	= 46.2 Cal. (calculated by second rule).
S (liquid) estimated	= 0.133 per kilogram.
	= 0.24 B. T. U. per pound.
B. P.	= 2100° (Fèry).
L. H. V.	= 2373 × 23 = 54,579 for Cu.
	= 858 Cal. per kg.

ZINC.

Sm (0 to t)	= 0.0906 + 0.000044t.
Melting point	= 420°.
Heat in solid metal at M. P.	= 45.2 Cal.
Heat in liquid metal at M. P.	= 67.8 Cal. (Person).
Latent heat of fusion	= 22.6 Cal. (observed).
Latent heat of fusion	= 22.4 Cal. (calculated by 2.1 T rule).
Latent heat of fusion	= 24.6 Cal. (calculated by second T rule).
S (liquid) (calculated)	= 0.1275 (from specific heat before fusion)
Boiling point	= 930°.
Latent heat of vaporization	= 23T = 27,670 Cal. for Zn = 65.
	= 425 Cal. per kilogram.
	= 765 B. T. U. per pound.
S (vapor) per cubic meter	= 0.225 Cal. (assumed).
per cubic foot	= 0.014 pound Cal.
per cubic foot	= 0.014 B. T. U.
per kilogram	= 0.076 Cal.
per pound	= 0.076 B. T. U.

GALLIUM.

Sm (12° to 23°)	= 0.079 (Bettendorf).
Melting point	= 30°.
Latent heat of fusion	= 19.1 Cal. (Berthelot).
Sm (liquid) (30° to 119°)	= 0.0802 (Berthelot).

ARSENIC.

Sm amorphous (21° to 65°)	= 0.0758 (Bettendorf and Wulner)
crystallized (21° to 65°)	= 0.083 (Bettendorf and Wulner).
Sublimation temperature	= 450° to As ⁴ .
Latent heat of sublimation	= 25T = 18,075 Cal. for As ⁴ = 300 = 60 Cal. per kilogram (calculated)

SELENIUM.

Sm (60° to 250°)	= 0.084 (Bettendorf and Wulner).
Melting point	= 125°.
Latent heat of fusion	= 13 Cal. per kilogram (second rule).
Boiling point	= 690° (Berthelot).
Latent heat of vaporization	= 22,150 Cal. for Se ² = 158 (calculated). = 140 Cal. per kilogram.

BROMINE.

Sm (solid) (-10° to -77°)	= 0.0843 (Regnault).
Melting point	= -7°.
Latent heat of fusion	= 16.2 Cal. (Regnault).
Sm (liquid) (-6° to +58°)	= 0.105 + 0.0011t.
Boiling point	= 58°.
Latent heat of vaporization	= 43.75 Cal. (Berthelot and Gier).
S (vapor) per kilogram	= 0.0555 Cal.
per pound	= 0.0555 B. T. U.
per cubic meter	= 0.80 Cal.

STRONTIUM.

Sm (solid) (0° to 100°)	= 6.4 Cal. per Sr = 87 (assumed). = 0.0735 Cal. per kilogram.
Melting point	= bright red heat.

ZIRCONIUM.

Sm (0° to 100°)	= 0.0662 (Mixer and Dana).
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COLUMBIUM.

Sm (0° to 100°)	= 6.4 Cal. per Cb. = 94 (assumed).
	= 0.068 Cal. per kilogram.
Melting point	unknown.

MOLYBDENUM.

Sm (5° to 15°)	= 0.0659 Cal. (De la Rive et Marcet)
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PALLADIUM.

Sm (0 to t)	= 0.0582 + 0.00001t (Violle).
Melting point	= 1500°.
Heat in solid metal at M. P.	= 109.8 Cal. (Violle).
Heat in melted metal at M. P.	= 146.1 Cal. (Violle).
Latent heat of fusion	= 36.3 Cal. per kilo. (observed).
	= 36.1 Cal. by calculation, rule 2.
	= 65.3 B. T. U. per pound.

SILVER.

Sm (0 to t) (up to 400°)	= 0.0555 + 0.00000943t.
(over 400°)	= 0.05758 + 0.0000044t + 0.000000006t ² (Pionchon).
Melting point	= 962°.
Heat in solid metal at M. P.	= 64.8 Cal. (Pionchon).
Heat in melted metal at M. P.	= 89.15 Cal. (Pionchon).
Latent heat of fusion	= 24.35 Cal. (Pionchon).
	= 23.5 Cal. (calculated by rule 2).
S (liquid) (962° to 1020°)	= 0.0748 Cal. (Pionchon).
	= 0.0782 (calculated from solid state at M. P.).
Boiling point (approximately)	= 1600° (V. Meyer).
Latent heat of vaporization	= 23T = 43,080 Cal. for Ag = 10S = 397 Cal. per kilogram. = 715 B. T. U. per pound.
S (vapor) per cubic meter	= 0.225 Cal. (assuming it mona- tomic).
per cubic foot	= 0.014 pound Cal.
per cubic foot	= 0.014 B. T. U.
per kilogram	= 0.046 Cal.
per pound	= 0.046 B. T. U.

CADMIUM.

Sm (0 to t)	= 0.0546 + 0.000012t (Naccari).
Melting point	= 321.7°.
Heat in solid metal at M. P.	= 18.81 Cal. (Naccari).
Heat in melted metal at M. P.	= 31.83 Cal. (Person).
Latent heat of fusion	= 13.02 Cal. per kilogram.
S (liquid) (calculated)	= 0.0623 (from S of solid at M. P.)
Boiling point	= 778° (Berthelot).
Heat in liquid metal at B. P.	= 50.26 Cal. (calculated).
Latent heat of vaporization	= 23T = 24,173 Cal. for Cd = 112 = 216 Cal. per kilogram. = 389 B. T. U. per pound.
S (vapor) per cubic meter	= 0.225 Cal. (assumed by rule).
per cubic foot	= 0.014 pound Cal.
per cubic foot	= 0.014 B. T. U.
per kilogram	= 0.0446 Cal.
per pound	= 0.0446 B. T. U.

TIN.

Sm (0 to t)	= 0.0560 + 0.000044t (Bede and Regnault).
Heat in solid metal at M. P.	= 14.34 Cal. (by above formula).
Heat in melted metal at M. P.	= 28.16 Cal. (Richards).
Latent heat of fusion	= 13.82 Cal. per kilogram. = 13.7 Cal. (by calculation, rule 2)
Sm (0 to t) (for t = 232° to 1000°)	= 0.06129 - 0.000010474t + 0.000000010345t ² + $\frac{14.37}{t}$ (Pionchon).
S (liquid) (250° to 340°)	= 0.0637 (Person).
Boiling point approximate	= 1550° (Carnelly).
Heat in liquid metal at B. P.	= 159 Cal. (Pionchon's formula).
Latent heat of vaporization	= 23T = 31,930 Cal. for Sn = 118 = 271 Cal. per kilogram. = 487 B. T. U. per pound.
S (vapor) per cubic meter	= 0.225 Cal. (assuming it mona- tomic).

S (vapor) per cubic foot	= 0.014 pound Cal.
per cubic foot	= 0.014 B. T. U.
per kilogram	= 0.0424 Cal.
per pound	= 0.0424 B. T. U.

ANTIMONY.

Sm (o to t)	= 0.04864 + 0.0000084t (Naccari).
Melting point	= 632°.
Heat in solid metal at M. P.	= 34.1 Cal. (by above formula).
Heat in melted metal at M. P.	= 74.3 Cal. (Richards).
Latent heat of fusion	= 40.2 Cal. per kilo. (Richards).
	= 15.8 Cal. (calculated by 2.1 T rule).
	= 16.0 Cal. (calculated by second rule).

There is a very large discrepancy here, which may be due to the value 74.3, determined by the writer being too high, or Naccari's results being too low. Further experiments by the writer have confirmed Naccari's results, and leave the latent heat of fusion of antimony anomolous. It should be, by two rules, about 16, and it appears to be 40. Possibly the water oxidizes it as it is poured melted into the calorimeter.

S (liquid) (632° to 830°)	= 0.0605 (Richards).
Boiling point	= 1600° (Biltz and V. Meyer).
Heat in liquid metal at B. P.	= 131.4 Cal. (calculated).
Latent heat of vaporization	= 23T = 43,080 Cal. for Sb = 120
	= 359 Cal. per kilogram.
	= 646 B. T. U. per pound.
S (vapor) per cubic meter	= 0.225 Cal. (assuming vapor mon-atomic).
per cubic foot	= 0.014 pound Cal.
per cubic foot	= 0.014 B. T. U.
per kilogram	= 0.0416 Cal.
per pound	= 0.0416 B. T. U.

TELLURIUM.

Sm (solid) (15° to 100°)	= 0.0525 Cal. (Fabre).
Melting point	= 455° (Richards).
Heat in solid metal at M. P.	= 27.3 Cal. (Richards).

Heat in melted metal at M. P.	= 46.3 Cal. (Richards).
Latent heat of fusion	= 19.0 Cal. (Richards).
	= 17.0 Cal. (calculated from rule 2)
	= 34.2 B. T. U. per pound.

IODINE.

Sm (solid) (9° to 98°)	= 0.05412 (Regnault).
Melting point	= 114°.
Latent heat of fusion (1 kilo.)	= 11.7 Cal. (Person).
Boiling point	= 183°.
Latent heat of vaporization	= 23.95 Cal. per kilogram (Fabre and Silberman).
S (vapor) 1 kilogram	= 0.03489 (constant pressure for I ²).
1 cubic meter	= 0.4088.
S (vapor) (above 1200°)	= 0.225 per cubic meter for I. = 0.0394 per kilogram.
Latent heat of change I ² = 2I	= 7,240 Cal. per formula, I ² . = 28.5 Cal. per kilogram of vapor.

BARIUM.

Sm (0°—100°)	= 0.05 (Mendeleeff).
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TANTALUM.

Sm (0°—100°)	= 6.4 per Ta = 183 (rule). = 0.035 Cal. per kilogram.
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TUNGSTEN.

Sm (6° to 15°)	= 0.035 Cal. per kilo. (De la Rive and Marcet).
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IRIDIUM.

Sm (0 to t)	= 0.0317 + 0.000006t (Violle).
Melting point	= 1950° (Violle).
Latent heat of fusion	= 2.1T = 4668 Cal. for Ir = 193. = 24.2 Cal. per kilogram. = 28.0 Cal. per kilogram by rule 2.
S (liquid)	= 0.055 (by rule, from solid at M. P.).

PLATINUM.

Sm (0 to t)	= 0.0317 + 0.000006t (Violle).
Melting point	= 1775° (Violle).
Heat in solid metal at M. P.	= 75.2 Cal. per kilogram (Violle).
Heat in melted metal at M. P.	= 102.4 Cal. per kilogram.
Latent heat of fusion	= 27.2 Cal. per kilogram.
	= 26.3 Cal. (calculated by rule 2).
S (liquid)	= 0.053 Cal. (by rule, from solid at M. P.).

GOLD.

S (from 0° to 600°)	= 0.0316—constant (Violle).
Heat in metal at 600° (to 0°)	= 18.96 Cal.
Sm (0 to t) (from 600 to M. P.)	= 0.0289 + 0.0000045t + $\frac{18.96}{t}$ (Violle)
Heat in solid metal at M. P.	= 34.63 Cal. (by above formula).
Heat in melted metal at M. P.	= 50.93 Cal. (Roberts-Austen).
Latent heat of fusion	= 16.3 Cal. per kilogram.
	= 15.5 Cal. (calculated by rule 2).
	= 14.4 Cal. (calculated by rule 1).
S (liquid)	= 0.0358 (from S of solid at M. P.)

MERCURY.

S (solid) (at—59°)	= 0.0319 (Regnault).
Sm (liquid) (—36° to 0°)	= 0.0333 (Pettersson).
Sm (0 to t) (0 to 250°)	= 0.03337—0.00000275t + 0.0000000667t ² (Naccari).
Melting point	= —40° C.
Latent heat of fusion	= 2.84 Cal. per kilo. at —40° (Person).
Boiling point	= 356°.
Latent heat of vaporization	= 67.8 Cal. per kilogram (Kur- batoff).
	= 72.5 Cal. (calculated by Trou- ton's rule).
S (vapor) per cubic meter	= 0.225 Cal. constant pressure.
per cubic foot	= 0.014 pound Cal.
per cubic foot	= 0.014 B. T. U.
per kilogram	= 0.025 Cal.
per pound	= 0.025 B. T. U.

THALLIUM.

Sm (17° to 100°)	= 0.03355 (Regnault).
Melting point	= 290°.
Latent heat of fusion	= 2.1T = 1182 Cal. for T1 = 204. = 5.8 Cal. per kilogram. = 5.8 Cal. per kilo. (by rule 2).
Boiling point	= 1700° (approximately) (Biltz and V. Meyer).
Latent heat of vaporization	= 45,380 Cal. by Trouton's rule, T1 = 204 = 224.5 Cal. per kilogram.
S (vapor) per cubic meter	= 0.225 Cal. (if monatomic).
per cubic foot	= 0.014 pound Cal.
per cubic foot	= 0.014 B. T. U.
per kilogram	= 0.024 Cal.
per pound	= 0.024 B. T. U.

LEAD.

Sm (0 to t)	= 0.02925 + 0.000019t (Bede and Regnault).
Melting point	= 326°.
Heat in solid metal at M. P.	= 11.6 Cal. (from above formula). = 11.6 Cal. (observed, Le Verrier).
Heat in liquid metal at M. P.	= 15.6 Cal. (Person).
Latent heat of fusion	= 4.0 Cal.
S (liquid) (335° to 430°)	= 0.0402 Cal. (Person). = 0.0418 Cal. (calculated from solid metal at M. P.).

BISMUTH.

Sm (0 to t)	= 0.0285 + 0.00002t (Regnault and Bede).
Melting point	= 267°.
Heat in solid metal at M. P.	= 9.0 Cal. (from above formula).
Heat in melted metal at M. P.	= 21.0 Cal. (Person).
Latent heat of fusion	= 12.0 Cal. (Person).
Sm (liquid) (280° to 360°)	= 0.0363 (Person).

THORIUM.

Sm (0 to 100°)	= 0.0276 (Nilson).
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URANIUM.

Sm (0 to 100°)

= 0.028 (Blümcke).

In several of the preceding instalments we have given the heats of formation of alloys and compounds and the thermophysics of the elements. Before passing to the thermophysics of alloys and compounds and problems involving their use, we will consider a few simple cases of the application of data so far given. Such include operations in which metals are melted or volatilized, or amalgams retorted. A few words may be in order, to clear the ground, regarding what is to be regarded as the efficiency of a furnace.

EFFICIENCY OF FURNACES.

Under this term we must distinguish a generic sense and a specific sense, the first referring to furnaces in which the object is to maintain a certain temperature for a certain time with the minimum consumption of fuel, the second, in which the object is to perform a certain thermal operation with the smallest consumption of fuel. In the first case, one furnace may be compared with another, and thus comparative efficiencies calculated; in the second case real or absolute efficiencies can be also calculated. A few examples will illustrate this difference, which is an essential difference as far as making calculations is concerned.

Cases of Specific Efficiency: Whenever it is desired to melt a metal for the purpose of casting it, a certain definite amount of heat must be imparted to the metal, and the ratio between this efficiently utilized heat and the heating power of the fuel consumed, is the efficiency of the furnace. If the furnace is electric the theoretical heat value of the electric energy used is the divisor. If, in addition to the heat required to raise the substances to the desired temperature, there is also heat absorbed in chemical reactions, this amount can be added in as usefully applied heat, and the sum of this and the heat in the final products be regarded as the total efficiently applied heat. If a blast furnace takes iron ore and furnishes us melted pig iron, the sum of the heat absorbed in the chemical decomposition of the iron oxide and the sensible heat in the melted pig iron is the efficiently applied heat, because it is the neces-

sary theoretical minimum required; all other items are more or less susceptible of reduction, but these are necessary items and, therefore, measure the net efficiency. If my dwelling requires 200 cubic feet of hot air per minute at 150° F. to keep it at 65° F., while the outside air is at 0° F., the ratio of the heat required to warm the 200 cubic feet of air from 0° F. to 150° F., to the calorific power of the fuel used per minute, measures the *specific* efficiency of the "heater;" the question whether this amount of hot air keeps the temperature of the rooms at 65° F. is a question of the *general* efficiency of the construction of the house.

Cases of Generic Efficiency: Such are those in which practically all the heat generated eventually leaves the furnace by radiation or conduction, or useless heat in waste gases; this is the case when a certain temperature has to be continuously maintained for a given time, and where the *time* element is the controlling one, and not any definite amount of thermal work is to be done. Examples are numerous: An annealing furnace, where steel castings, let us say, are to be kept at a red heat for two days, or a brick kiln, where several days slow burning are required, or a puddling furnace, where the melted iron must be held one to two hours to oxidize its impurities. In all these cases we may say that one furnace keeps its contents at the right heat for the right time with so much fuel, another does the same work with 10 or 25 per cent. less fuel, and is, therefore, 10 or 25 per cent. more efficient; but we cannot, in the nature of the case, speak of the absolute or specific efficiency of the furnace, because there is no definite term, expressible in calories, to compare with the thermal power of the fuel.

In many cases the two efficiencies are mixed in the same process or operation, and then the calculation of absolute or specific efficiency can be made for that portion of the operation wherein a certain definite amount of thermal work is done. Thus, in an annealing kiln, 50 tons of castings may be brought up to annealing heat in 24 hours, starting cold, and the heat absorbed by the castings compared with the calorific power of the coal burnt during this period, is a measure of the real efficiency of this part of the operation. During the rest of the operation, while the castings are simply kept at annealing heat,

there can be no calculation of the absolute or specific efficiency of the furnace, because one of the terms necessary for the comparison has disappeared, in that part of the process we can only speak of relative efficiency compared to some other furnace doing a similar operation.

It goes, almost without saying, that we can, of course, apply the conception of efficiency in its relative or general sense to the whole operation or to any part of it

Problem 6.

The Rockwell Engineering Co. state in their current advertisements that their regenerative oil-burning furnace melts 100 pounds of copper with the consumption of less than 1.5 gallons of oil. Assume that 1.5 gallons of oil is used, and that the copper is heated from 25° C. to melted metal 100° C. above its melting point.

Required: The "efficiency" of the furnace; *i.e.*, its specific efficiency as calculated from the net heat utilized.

Solution: One gallon of fuel oil averages in weight 7.5 pounds, and its calorific power 11,000 Calories per kilogram, or 11,000 pounds Calories per pound. The calorific power of the fuel used in melting 100 pounds of copper is therefore:

Heat generated $11,000 \times 7.5 \times 1.5 = 82,500 \times 1.5 = 123,750$ pound Calories.

The heat imparted to the copper is as follows, taking the data from Article V. of these calculations: (p. 68.)

Heat in 1 lb. melted copper at melting point	=	162 lb. Cal.
Heat in 1 lb. solid copper at 25° C.	=	2 "
Heat required to just melt the copper	=	160 "
Heat to superheat liquid copper 100° C.		
	$0.133 \times 100 =$	13 "
Total heat expended on each pound of copper	=	173 "
Heat usefully applied per 100 pounds	=	17,300 "

$$\text{Net efficiency of furnace} = \frac{17,300}{123,750} = 0.14 = 14\%$$

It is proper to remark that although this efficiency appears low, yet it is considerably greater than is attained in simple melting holes or wind furnaces, and yet the calculations show

what a large margin for improvement and greater efficiency exists in even some of the best and relatively most efficient metallurgical furnaces.

Problem 7.

In the distillation of silver amalgam in iron retorts, 1000 kilos, of amalgam, containing 200 kilos. of silver, is retorted with the consumption of 550 kilos. of wood, the mercury vapor passes off at an average temperature of 450° C., and the silver is raised towards the end of the operation to 800° C., in order to expel the last of the mercury. Assume the calorific power of the wood 3000 Calories.

Required: The net efficiency of the furnace.

Solution: The heating power of the wood is $550 \times 3000 = 1,650,000$ Calories.

The heat utilized is that absorbed in separating the silver from the mercury plus the sensible heat in the mercury vapor at 450°, plus the sensible heat in the silver at 800°. These are calculated as follows:

Heat to decompose amalgam = 2470 Calories per 108 kilos. of silver = $200 \times (2470 \div 108) = 200 \times 229 = 45,800$ Calories.

Heat in silver at 800°, using Pionchon's formula, is $800 [0.05758 + 0.0000044 (800) + 0.000000006 (800)^2] \times 200 = 10,390$ Calories.

Heat in 800 kilos. of mercury vapor at 450° is

(a) heat to boiling point (Niccari)

356 $[0.03337 - 0.00000275 (356) -$

$0.0000000667 (356)^2] \times 800$

= 14,699 Cal.

(b) heat to vaporize 77.5×800

= 62,000 "

(c) heat in vapor at 450° =

$0.025 \times (450 - 356) \times 800$

= 1,880 "

Total = 78,579 "

Heat usefully applied:

In decomposing amalgam

= 45,800 "

In mercury vapor, as sensible heat

= 78,590 "

In silver, as sensible heat

= 10,390 "

Total = 134,769 "

Efficiency of furnace = $\frac{134,769}{1,650,000} = 0.082 = 8.2\%$.

72.5
67.8
1.174

Problem 8.

In a zinc works, impure zinc is refined by redistillation in fire-clay retorts, a bank of retorts distilled 970 kilos. of zinc with the expenditure of 912 kilos. of small anthracite coal. Assume that the zinc vapors pass out of the muffles at the boiling point (930°).

Required: (1) The net efficiency of the furnace.

(2) The electrical power which would be required, in horse-power-hours, to do the same work, assuming the heating efficiency of the electric furnace is 75 per cent.

Solution: (1) The small anthracite may be assumed to have a calorific power of 7850 Calories; therefore, the total heat which should be developed is $7850 \times 912 = 7,159,200$ Calories. The heat in 1 kilo. of zinc in the state of vapor at its boiling point can be calculated from the thermophysical data supplied for zinc as:

(a) In solid zinc to melting point (420°).....	47.34 Cal.
(b) Latent heat of fusion.....	22.61 "
(c) Heat in melted zinc to boiling point (930°)....	65.05 "
(d) Latent heat of vaporization.....	370.15 "
	Total 505.15 "

Heat required for 970 kilos. = 489,995 "

$$\text{Efficiency of furnace} = \frac{489,995}{7,159,200} = 0.068 = 6.8\%$$

(2) One electric horse-power-hour = 644.0 Cal.
Efficiently applied heat = $644 \times .75$ = 483.0 "

Electric horse-power-hours required = $\frac{489,995}{483} = 1013$ E.H.P hours

One metric ton of zinc requires $\frac{1013}{0.970} = 1044$ E.H.P. hours.

Cost of power, at \$20.00 per E. H. P. year = $\frac{20.00}{8766} \times 1044 = 0.00228 \times 1044 = \2.38 .

This cost of electric power would replace the use of $\frac{0.912}{0.970}$ metric tons of small anthracite, equal to a cost of \$2.53 for

electric power sufficient to replace a metric ton of coal for this purpose.

Many other examples could be given of the technical use of the thermophysical data concerning the elements, but the problems given illustrate the methods of calculation.

When one is acquainted with some of the ordinary metallurgical operations, such as melting and distilling the metals, it is surprising to notice how little is known or thought of the efficiency or lack of efficiency of the furnaces used. One man melts 100 pounds of metal by the use of 150 pounds of coal, he builds a new furnace and does it more cheaply by using 100 pounds of coke, which is certainly relatively more efficient; but it is seldom that the operator knows that in one case he is getting probably only 7 per cent. efficiency from his fuel and in the other case only 10 per cent. It is the knowledge of these absolute efficiencies which tells the practical man just what he is accomplishing, and shows him how much room there still remains for improvement.

THERMOPHYSICS OF ALLOYS.

There does not exist, in technical literature, much data of this nature concerning alloys. There is here a wide and interesting field for metallurgical research, whose cultivation would yield results both of high practical and high theoretical interest, and yet it is comparatively untouched. What is wanted is complete data concerning the specific heat of solid and liquid alloy, and latent heat of fusion. These, combined with the determination of the heat evolved in the alloying, would furnish a sound basis for a practical theory of alloys, besides enabling workers with these alloys to control the efficiency of their furnaces and, in general, to know with scientific exactness what they are accomplishing.

ALLOYS OF TIN AND LEAD.

Per Cent. of Tin.	Sm.	Latent Heat of Fusion.
4.8 (Pb ¹⁰ Sn)	5.5 (Mazotto)
10.2 (Pb ⁵ Sn)	8.0 at 307° (Spring)
12.5 (Pb ⁴ Sn)	8.3 at 292° (Spring)

Per Cent. of Tin.	Sm.	Latent Heat of Fusion.
16.0 (Pb ³ Sn)	9.1 at 289° (Spring)
22.2 (Pb ² Sn)	9.5 at 270° (Spring)
		7.9 (Mazotto)
36.3 (PbSn)	0.04073 (12°—99°)	11.6 at 241° (Spring)
	(Regnault)	
		9.4 (Mazotto)
50.0 = total heat to 0° in 1 kilo.		
	melted metal	18.0 from 202° (Ledebur)
53.3 (PbSn ²)	0.04507 (10°—99°)	10.5 at 197° (Mazotto)
	(Regnault)	
63.1 (PbSn ³)	15.5 at 179° (Spring)
69.5 (PbSn ⁴)	17.0 at 188° (Spring)
83.0 = total heat to 0° in 1 kilo.		
	melted metal	21.5 from 205° (Ledebur)
90.1 (PbSn ¹⁰)	12.9 (Mazotto)

ALLOYS OF TIN AND BISMUTH.

Per Cent. of Tin.	Sm.	Latent Heat of Fusion.
6.7 (Bi ⁸ Sn)	11.4 Cal. (Mazotto)
22.1 (Bi ² Sn)	11.2 Cal. (Mazotto)
36.2 (BiSn)	0.0400 (20°—99°)	11.6 Cal. (Mazotto)
	(Regnault)	
53.1 (BiSn ²)	solid, 0.0450	11.6 (Cal. Mazotto)
	(Regnault)	
	liquid, 0.0454	
	(146°—275°) Person	
69.1 (BiSn ⁴)	11.1 Cal. at 140°
		(Mazotto)
82.7 (BiSn ⁸)	12.6 Cal. (Mazotto)
90.1 (BiSn ¹⁶)	12.8 Cal. (Mazotto)

ALLOYS OF TIN AND ZINC.

Per Cent. of Tin.	Sm.	Latent Heat of Fusion.
78.4 (ZnSn ²)	23.5 Cal. (Mazotto)
92.7 (ZnSn ⁷)	16.2 Cal. at 197°
		(Mazotto)
95.6 (ZnSn ¹²)	16.3 Cal. (Mazotto)
97.3 (ZnSn ²⁰)	15.1 Cal. (Mazotto)

ALLOYS OF TIN AND COPPER.

Bell metal (20 per cent. tin) Sm (14° — 98°) = 0.0862 (Regnault).

Bronze (15 per cent. tin).

Total heat in melted metal (to 0°) = 130 Cal. (Ledebur).

If strongly superheated = 143.5 Cal. (Ledebur).

ALLOYS OF TIN AND ANTIMONY.

Britannia metal (90 per cent. tin) requires to melt it, starting cold, 28.0 Calories per kilogram (melting point 236°); with 82 per cent. of tin, 25.7 Calories; melting point 205° (Ledebur).

ALLOYS OF TIN, BISMUTH AND ANTIMONY.

BiSn^2Sb (bismuth 34.3, tin 41.9, antimony 23.8 per cent.).

Sm (15° — 100°) = 0.0462 (Regnault).

ALLOY OF TIN, BISMUTH, ANTIMONY AND ZINC.

$\text{BiSn}^2\text{SbZn}^2$ (bismuth 29.8, tin 34.0, antimony 17.3, zinc 18.9 per cent.).

Sm (15° — 100°) = 0.0566 (Regnault).

ALLOYS OF LEAD AND BISMUTH.

Per Cent. of Lead.	Sm.	Latent Heat of Fusion.
11.1 (PbBi^8)	10.2 (Mazotto)
33.2 (PbBi^2)	6.4 (Mazotto)
39.9 (Pb^2Bi^3)	solid, 0.03165 (16° — 99°) Person. liquid, 0.03500 (144° — 358°) Person	
42.7 (Pb^3Bi^4)	4.7 at 127° (Mazotto)
49.9 (PbBi)	4.0 (Mazotto)
66.6 (Pb^2Bi)	3.6 (Mazotto)
88.8 (Pb^8Bi)	4.9 (Mazotto)

ALLOYS OF LEAD AND ANTIMONY.

With 63.0 per cent of lead, Sm (10° — 98°) = 0.0388 (Regnault)

With 82.0 per cent. of lead, heat in 1 kilo. melted metal = 15.6 Calories (Ledebur).

With 90.0 per cent. of lead, total heat in 1 kilo. melted metal = 13.8 Calories (Ledebur).

ALLOYS OF LEAD, TIN AND BISMUTH.

D'Arcet's Alloy, containing 32.5 lead, 18.5 tin, 48.7 bismuth

Sm solid (5°—65°)	= 0.0372 (Mazotto)
Sm solid (12°—50°)	= 0.049 (Person).
Sm solid (14°—80°)	= 0.060 (Person).
Sm liquid (107°—136°)	= 0.047 (Person).
Sm liquid (120°—150°)	= 0.0399 (Mazotto).
Sm liquid (136°—300°)	= 0.0360 (Person).
Latent heat of fusion	= 5.96 Cal. at 96° (Person).
	= 5.77 Cal. at 99° (Mazotto).

Rose's Alloy, containing 24.0 lead, 27.3 tin, 48.7 bismuth:

Sm solid (5°—65°)	= 0.375 (Mazotto).
Sm fluid (119°—338°)	= 0.0422 (Person).
Latent heat of fusion	= 6.85 Cal. at 99° (Mazotto).

Fusible Alloy, containing 31.8 lead, 36.2 tin, 32.0 bismuth:

Sm solid (18°—52°)	= 0.0423 (Person).
Sm solid (11°—98°)	= 0.0448 (Regnault).
Sm fluid (143°—330°)	= 0.0460 (Person).
Latent heat of fusion	= 7.63 Cal. at 145° (Person).

Wood's Alloy, containing 25.8 lead, 14.7 tin, 52.4 bismuth:
7 cadmium:

Sm solid (5°—50°)	= 0.0352 (Mazotto).
Sm fluid (100°—150°)	= 0.0426 (Mazotto).
Latent heat of fusion	= 7.78 Cal. at 75° (Mazotto).

Lipowitz's Alloy, containing 25.0 lead, 14.2 tin, 50.7 bismuth,
10.1 cadmium:

Sm solid (5°—50°)	= 0.0345 (Mazotto).
Sm fluid (100°—150°)	= 0.0426 (Mazotto).
Latent heat of fusion	= 8.40 Cal. at 75° (Mazotto).

ALLOYS OF COPPER AND ZINC.

<i>Red Brass</i>	S at 0° = 0.0899 (Lorenz)
	S at 50° = 0.0924 (Lorenz)
(Copper 85%)	S at 75° = 0.0940 (Lorenz)
<i>Yellow Brass</i>	S at 0° = 0.0883 (Lorenz)
	at 50° = 0.0922 (Lorenz)
(Copper 65%)	at 175° = 0.0927 (Lorenz)

Heat in 1 kilo. of melted, somewhat superheated, brass =
130 Calories (Ledebur).

ALLOYS OF COPPER, ZINC AND NICKEL.

German Silver:

$$(74\text{Cu. } 20\text{Zn. } 6\text{Ni}) \text{ Sm}(0-t) = 0.0941 + 0.0000053t$$

(Tomlinson)

ALLOYS OF COPPER AND ALUMINIUM.

$$\text{Copper } 88.7\% \text{ Sm } (20^\circ-100^\circ) = 0.10432 \text{ (Luginin)}$$

ALLOYS OF SILVER AND PLATINUM.

$$\text{Silver } 66.7\% \text{ Sm } (0-t) = 0.04726 + 0.0000138t \text{ (Tomlinson).}$$

ALLOYS OF MERCURY AND TIN.

$$\begin{aligned} \text{HgSn } (37.1\% \text{ Sn}) \text{ Sm } (-30^\circ-15^\circ) &= 0.04083 \text{ (Schüz)} \\ &(-25^\circ-15^\circ) = 0.04218 \text{ (Schüz)} \\ &(22^\circ-99^\circ) = 0.07294 \text{ (Regnault)} \\ \text{HgSn } (54.1\% \text{ Sn}) \text{ Sm } (25^\circ-99^\circ) &= 0.06591 \text{ (Regnault)} \\ \text{HgSn}^5(74.7\% \text{ Sn}) \text{ Sm } (-16^\circ-15^\circ) &= 0.05039 \text{ (Schüz)} \end{aligned}$$

ALLOYS OF MERCURY AND LEAD.

$$\begin{aligned} \text{Pb Hg } (50.9\% \text{ Pb}) \text{ Sm } (-69^\circ-20^\circ) &= 0.03458 \text{ (Schüz)} \\ &\text{Sm } (23^\circ-99^\circ) = 0.03827 \text{ (Regnault)} \\ \text{Pb}^2\text{Hg } (67.4\% \text{ Pb}) \text{ Sm } (-72^\circ-20^\circ) &= 0.03348 \text{ (Schüz)} \end{aligned}$$

ALLOYS OF CADMIUM AND TIN.

$$\begin{aligned} \text{CdSn}^2(67.8\% \text{ Sn}) \text{ Sm } (-77^\circ-20^\circ) &= 0.05537 \text{ (Schuz)} \\ \text{whence we have Sm } (0-t) &= 0.0557 + \\ &0.00000366t \text{ (Schüz)} \end{aligned}$$

ALLOYS OF IRON AND CARBON.

$$\begin{aligned} \text{Soft Steel } (0.15\% \text{ carbon}) \text{ Sm } (20^\circ-98^\circ) &= 0.1165 \text{ (Regnault).} \\ \text{Hard Steel } (1.00\% \text{ carbon}) \text{ Sm } (20^\circ-98^\circ) &= 0.1175 \text{ (Regnault).} \\ \text{Total heat in 1 kilo melted steel at } 1350^\circ &= 300 \text{ Calories} \\ \text{(Ledebur).} \\ \text{Cast Iron } (4.0\% \text{ carbon}) \text{ Sm } (0-1200^\circ) &= 0.175. \\ &\text{Sm } (0-t^\circ) = 0.12 + 0.000046t \\ \text{Total heat in 1 kilo. melted at } 1200^\circ &= 245 \text{ Calories (Ledebur).} \\ \text{Total heat in 1 kilo. coming from blast furnace} &= 250 \text{ to } 325 \\ \text{Calories (Akermann).} \end{aligned}$$

Problem 9.

A steel-melting crucible contains 110 pounds of steel, which is melted in a wind furnace with the use of 150 pounds of coke. Assume the coke to be 90 per cent. fixed carbon, and the steel to be superheated 100° C. above its melting point.

Required: The net efficiency of the furnace.

Solution: The calorific power of the coke may be assumed as 90 per cent. that of pure carbon, and therefore:

$$= 150 \times (8100 \times 0.90) = 150 \times 7290 = 1,093,500 \text{ lb. Cal.}$$

Heat in steel at melting point:

$$110 \times 300 \text{ (Ledebur)} = 33,000$$

Heat to superheat 100°:

$$110 \times 100 \times 0.15 \text{ (assumed)} = 1,650$$

$$\text{Total } \frac{34,650}{34,650} \text{ lb. Cal.}$$

$$\text{Efficiency of furnace} = \frac{34,650}{1,093,500} = 0.032 = 3.2\%$$

Problem 10.

A Siemen's regenerative furnace holds eighteen steel crucibles, each containing 100 pounds of steel. Assume that the efficiency of utilization of the heat for melting the steel is 5 per cent., and that the furnace is fed by natural gas, having a calorific power of 512-pound Calories per cubic foot.

Required: The number of cubic feet of natural gas required per furnace heat of eighteen crucibles = 1800 pounds of cast steel.

Solution: Heat in steel = $1800 \times 315 = 567,000$ lb. Cal.

Heating power of gas required = $\frac{567,000}{0.05} = 11,340,000$ lb. Cal.

Cubic feet of gas required = $\frac{11,340,000}{512} = 22,150$ cubic feet.

Gas required per ton of steel, 2000 lbs. = 24,610 cubic feet.

Cost of gas, at \$0.08 per 1000 cubic feet = \$1.97.

Problem 11.

In a malleable-casting foundry the pig iron is melted in a reverberatory air furnace, 3000 kilos. being melted in two hours

by the combustion of 1200 kilos. of bituminous coal, having a calorific power of 8500 Calories.

Required: The melting efficiency of the furnace.

Solution: Calorific power of coal used:

$$1200 \times 8500 = 10,200,000 \text{ Calories.}$$

Heat in melted iron at foundry heat:

$$3000 \times 250 \text{ (Ledebur)} = 750,000 \text{ Calories.}$$

$$\text{Efficiency of furnace} = \frac{750,000}{10,200,000} = 0.0735 = 7.35\%$$

Problem 12.

In an iron foundry cupola 14 metric tons of pig iron are melted in one hour, using 1.5 tons of coke (90 per cent. carbon). The gases passing away contain by volume CO 13 per cent., CO² 13 per cent., nitrogen 76 per cent., and leave the cupola at 500° C. The body of the cupola is 1.5 meters in diameter outside and 4 meters high.

Required:

- (1) The net melting efficiency of the cupola.
- (2) The proportion of the calorific power of the coke lost.
 - (a) By the sensible heat of the hot gases escaping.
 - (b) By the imperfect combustion of the coke.
 - (c) By radiation from bottom and walls of the cupola.
- (3) The amount of heat in Calories radiated, on an average, from each square meter of outside surface per minute.

Solution:

- (1) Calorific power of the coke;

$$1500 \times 0.90 \times 8100. = 10,935,000 \text{ Calories.}$$

Heat in melted iron:

$$14,000 \times 250 \text{ (Ledebur)} = 3,500,000 \text{ Calories.}$$

$$\text{Efficiency of melting} = \frac{3,500,000}{10,935,000} = 0.32 = 32\%$$

- (2, a) Weight of carbon escaping = $1500 \times 0.90 = 1350$ kilos.

$$\text{Volume of CO and CO}^2 \text{ escaping} = \frac{1350}{0.54} = 2500 \text{ m}^3$$

(Because 1 m³ of either gas carries 0.54 kilos. C.)

$$\text{Volume of escaping gas} = \frac{2500}{0.13+0.13} = 9615 \text{ m}^3$$

Volume of nitrogen (by difference) = 7115 m³

Sensible heat of nitrogen and CO

$$(7115+1250) \times [0.303 (500) + 0.000027 (500)^2] = 1,323,760 \text{ Cal.}$$

Sensible heat of CO²

$$1250 \times [0.37 (500) + 0.00022 (500)^2] = 300,000 \text{ "}$$

Total sensible heat in gases = 1,623,760 "

Proportion of calorific power of the fuel thus lost:

$$= \frac{1,623,760}{10,935,000} = 0.1485 = 14.85\%$$

(2, b) Volume of CO escaping = 1250 m³

Caloric power of this gas = 1250 × 3062 = 3,827,500 Cal.

Proportion of calorific power of the fuel thus lost:

$$= \frac{3,827,500}{10,935,000} = 0.35 = 35\%$$

(2, c) Heat in pig iron = 3,500,000 Cal.

Heat in waste gases = 1,623,760 "

Lost by imperfect combustion = 3,827,500 "

Accounted for = 8,951,260 "

Calorific power of the coke = 10,935,000 "

Difference, loss by radiation = 1,983,740 "

Proportion of calorific power of the fuel thus lost:

$$= \frac{1,983,740}{10,935,000} = 0.1815 = 18.15\%$$

(3) Area of bottom of cupola = (1.5)² × 0.7854 = 1.77 m²

Area of sides of cupola = 1.5 × 3.14 × 4 = 18.85 m²

Total radiating area = 20.62 m²

Heat radiated per sq. m. per hour = $\frac{1,983,740}{20.62}$ = 96,200 Cal.

Heat radiated per sq. m. per min. = $\frac{96,200}{60}$ = 1,603 "

In general, we may state that the net efficiency in melting, etc., of metals is very various, from, say, 2 or 3 per cent. in a crucible steel-melting wind furnace to about 10 or 15 per cent. in reverberatory furnaces, 20 to 30. per cent in regenerative open-hearth furnaces, 30 to 50 per cent. in shaft furnaces, where material to be heated and fuel burned are in direct contact with each other, 50 to 75 per cent. in steam boilers and hot-blast stoves, and 60 to 85 per cent. in large electrical furnaces.

CHAPTER V.

THERMOPHYSICS OF CHEMICAL COMPOUNDS.

The metallic oxides are the most important compounds occurring in metallurgy, together with the oxides of hydrogen, carbon and of sulphur, arsenic and antimony, which are formed during combustion and in roasting operations. We do not include as oxides those combinations of two or more oxides in chemical proportions, such as of silica with metallic oxides, which form oxygen salts or ternary oxygen compounds. They will be separately discussed. In the following lists *Sm*, as before, means the mean specific heat per kilogram, in large Calories (or per pound in lb. Cal.) in the range of temperature given; *S* means actual specific heat at the temperature given, and *Q* is the quantity of heat absorbed in fusion or volatilization or in passing through any designated range of temperature. Temperatures are given only in centigrade degrees, excepting that *t* signifies Fahrenheit temperature; volumes of gases are understood as being at 0° C. and 760 m.m. pressure, unless distinctly stated otherwise.

OXIDES.

Hydrogen Oxide, H²O:

Ice	<i>Sm</i> (−78°—0°)	= 0.463 (Regnault).
	(−30°—0°)	= 0.505 (Person).
Water—	<i>Sm</i> (0°—100°)	= 1 + 0.00015 <i>t</i> (Pfaundler).
	<i>S</i> (at 15°)	= 1.0045 (Pfaundler).
	<i>S</i> (at 0°)	= 1.0000 (assumed).

In all metallurgical calculations it will be sufficiently exact to assume the specific heat of water at ordinary temperatures as unity. In heating to the boiling point, from zero, 101.5 Calories are absorbed.

Gas Sm (0° to t°)	
1 m ³ up to 2000°	= 0.34 + 0.00015t (Mallard and Le Chatelier).
1 m ³ 2000°—4000°	= 0.48 + 0.00017t (Vielle).
1 ft ³ up to 2000°	= 0.021 + 0.000009t—lb. Cal.
1 ft ³ 2000°—4000°	= 0.030 + 0.000011t—lb. Cal.
1 kilo. up to 2000°	= 0.42 + 0.000185t—Cal.
1 kilo. 2000°—4000°	= 0.59 + 0.00021t Cal.
1 lb. up to 2000°	= 0.42 + 0.000185t—lb. Cal.
1 lb. 2000°—4000°	= 0.59 + 0.00021t—lb. Cal.
1 ft ³ up to 3600° F.	= 0.021 + 0.000005t B. T. U.
1 ft ³ 3600°—7200° F.	= 0.030 + 0.000006t B. T. U.
1 lb. up to 3600° F.	= 0.42 + 0.000103t B. T. U.
1 lb. 3600°—7200° F.	= 0.59 + 0.00012t B. T. U.

Above figures are for water vapor as it exists in almost all metallurgical problems, as true gas far removed from its maximum tension at any given temperature. When the water vapor exists as saturated steam under its maximum tension, as in a steam boiler, it is recommended to consult tables giving the total heat in steam at any temperature condensing to liquid water at 0°, or to use Regnault's formula for the same:

$$Q = 606.5 + 0.305t$$

which expresses the amount of heat required to convert 1 kilogram of water, liquid at 0°, into steam at its maximum pressure at the temperature t . A little reflection will show that the above formula amounts to taking the specific heat of a kilogram of saturated steam, under a constantly *increasing pressure*, as

$$Q = 0.305t$$

or under increasing pressure

$$Sm = 0.305$$

or per cubic meter (0.81 kilos.)

$$Sm = 0.247$$

These figures apply to boiler practice only. In cases where water is evaporated at or below 100° C., and converted afterwards into steam at a high temperature, I recommend first calculating the heat required to convert the water into vapor at 0° (606.5 Cal.) and then treating the vapor afterwards as true gas, by the formulæ of Mallard and Le Chatelier. This puts water vapor at once, from the beginning, on the same footing as all the other gases, and greatly simplifies all subsequent calculations, without introducing any unnecessary errors.

Latent heat of fusion	= 80 Cal. (Bunsen).
Latent heat of vaporization	= 606.5 Cal. at 0° (Regnault).
	= 600.0 Cal. at 10°.
	= 537.0 Cal. at 100° (to vapor at 760 m m).
Total heat in saturated steam	= 606.5 + 0.305t (Regnault).

Most metallurgical problems which have to do with converting moisture in fuel, ores, etc., into vapor, are concerned with the evaporation of the water far below 100° by means of dry gases, into which the water vapor enters at a partial pressure, which is only a small fraction of atmospheric pressure. The problem is, in these cases, to find how much heat is necessary to convert the water into vapor at the low temperature corresponding to such low pressure. By finding the temperature corresponding to said partial pressure, as a maximum tension, applying Regnault's formula, we get the heat absorbed in producing the vapor at that temperature. We can then add to this the heat required to raise the vapor up to the higher temperature at constant pressure, using Mallard and Le Chatelier's formulæ.

Example: Wet peat is dried in a kiln by hot air, the issuing air being at 50° C. and the tension of the moisture in it 25 millimeters. How much heat is absorbed in latent heat, and how much as sensible heat per 1 kilogram of water evaporated?

Solution: The tension, 25 millimeters, is the maximum tension of aqueous vapor at 26° (Tables). To change 1 kilogram of water at zero to saturated vapor at 26° requires, according to Regnault's formula, $606.5 + 0.305(26) = 614$ Calories. (The real latent heat of vaporization at 26° is, therefore, $604 - 26 = 588$ Calories.) The heat required to evaporate 1 kilogram of water under the conditions of the peat kiln is therefore:

Heat to produce vapor at 25 m.m. (26°)	= 614.0 Calories.
Heat to raise vapor from 26° to 50° (constant pressure) = $[0.42 + 0.000185(50 + 26)] \times$ (50 - 26)	= 10.4 "
	Total = 624.4 "

In most cases of drying or evaporation the results will be sufficiently accurate by assuming the water first evaporated at

0°, with latent heat of evaporation 606.5 Calories, and then raised as gas to the end temperature. The difference between this method and the above will be small, where the temperature of the issuing gas is below 100° and the proportion of vapor in it small; where the temperature of issuing gas is high and the amount of vapor in it large, the more exact method should be used. To facilitate this, the maximum tension of aqueous vapor for temperatures up to 100° is here given:

Temperature C°.	Max. Tension. mm. of Hg.	Temperature C°.	Max. Tension. mm. of Hg.
0°	4.6	50°	92.0
5°	6.5	55°	117.5
10°	9.1	60°	148.9
15°	12.7	65°	187.1
20°	17.4	70°	233.3
25°	23.5	75°	288.8
30°	31.5	80°	354.9
35°	41.8	85°	433.2
40°	54.9	90°	525.5
45°	71.4	95°	633.7
50°	92.0	100°	760.0

Beryllium Oxide, Be²O³

Sm (0°—100°) = 0.2471 (Nilson and Pettersson).

Boric Oxide, B²O³:

Sm (16°—98°) = 0.2374 (Regnault).

Carbonous Oxide, CO:

Sm (0° to t°) 1 m³ up to 2000° = 0.303 + 0.000027t (Mallard and Le Chatelier).

1 m³ 2000°—4000° = 0.2575 + 0.000072t (Berthelot).

1 ft³ up to 2000° = 0.0189 + 0.0000017t lb. Cal.

1 ft³ 2000°—4000° = 0.0161 + 0.0000045t lb. Cal.

1 kilo. up to 2000° = 0.2405 + 0.0000214t Cal.

1 kilo. 2000°—4000° = 0.2044 + 0.000057t Cal.

1 lb. up to 2000° = 0.2405 + 0.0000214t lb. Cal.

1 lb. 2000°—4000° = 0.2044 + 0.000057t lb. Cal.

1 ft.³ up to 3600° F. = 0.0189 + 0.0000009t B. T. U.

1 ft. 3600—7200° F. = 0.0161 + 0.0000025t B. T. U.

1 lb. up to 3600° F. = 0.2405 + 0.0000119t B. T. U.

1 lb. 3600°—7200° F. = 0.2044 + 0.000032t B. T. U.

Carbonic Oxide, CO²:

There has been much doubt about the specific heat of this gas, and several experimenters have given it particular attention. Direct combustion of CO to CO² in air has recently given Mallard and Le Chatelier a directly-observed temperature of 2050°, while the formula, which has so far been considered by us as the most reliable ($Sm = 0.37 + 0.00027t$), leads to 1947°. After renewed consideration of the whole subject the writer considers the best values those given below, because by accepting these they will agree with the observed temperature of combustion, 2050°. We will hereafter use these values instead of the one just above. Above 2000° the values of Berthelot and Vielle are the only ones to be used.

Sm (0° to t°) 1 m³ up to

2050°	= 0.37 + 0.00022t (calculated by Richards).
1 m ³ 2000°—4000°	= 0.815 + 0.0000675t (Vielle).
1 ft ³ up to 2050°	= 0.023 + 0.000014t lb. Cal.
1 ft ³ 2000°—4000°	= 0.051 + 0.0000042t lb. Cal.
1 kilo. up to 2050°	= 0.19 + 0.00011t Cal.
1 kilo. 2000°—4000°	= 0.42 + 0.000034t Cal.
1 lb. up to 2050°	= 0.19 + 0.00011t lb. Cal.
1 lb. 2000°—4000°	= 0.41 + 0.000034t lb. Cal.
1 ft ³ up to 3700° F.	= 0.023 + 0.000008t B. T. U.
1 ft ³ 3600°—7200° F.	= 0.051 + 0.0000023t B. T. U.
1 lb. up to 3700° F.	= 0.19 + 0.00006t B. T. U.
1 lb. 3600°—7200° F.	= 0.41 + 0.000019t B. T. U.

In all the above formulæ, Q from t° to 0° is equal to Sm multiplied by t; e.g., Q (0° to t°) 1 m³ to 2050° = 0.37t + 0.00022t².

Nitrogen Peroxide, NO²:

Sm (27°—280°) 1 m ³	= 1.35 (Berthelot and Ogier).
1 kilo.	= 0.65 Cal.

Magnesium Oxide, MgO:

Sm (24°—100°)	= 0.2440 (Regnault).
Sm (0°—t°)	= 0.2420 + 0.000016t (assumed).
Mg (OH ²) Sm (19°—50°)	= 0.312 (Kopp).

Aluminium Oxide, Al²O³ (alumina, corundum):

Sm (0° to t°)	= 0.2081 + 0.0000876t (constant by Regnault, coefficient of t by Richards, on a corundum crystal tested up to 1200°).
Melting point	= about 2200°.
Latent heat of fusion	= 2.1T = 5,193 Cal. for Al ² O ³ . = $\frac{5,193}{102}$ = 509 Cal. per kilo
Heat in solid at 2200°	= 932 Cal. by formula.
Total heat in liquid to 0°	= 1,390 Cal.
Specific heat, liquid	= 0.593 = specific heat of solid at M. P.

Silicon Oxide, SiO² (silicon, quartz):

Sm (0° to t°)	= 0.1833 + 0.000077t (constant by Regnault, coefficient of t by Richards, on clear quartz up to 1200°).
Latent heat of fusion (at 1750°)	= 135 Cal. (Voigt).
Melting point	= 1900° (Boudouard).
Latent heat of fusion	= 2.1T = 4,563 Cal. for SiO ² . = $\frac{4,563}{60}$ = 76.1 Cal. per kilo. = 135 Cal. (Voigt).
Heat in solid at 1900°	= 626 Cal. by formula.
Total heat in liquid to 0°	= 761 Cal.
Specific heat, liquid	= 0.476 = specific heat of solid at M. P.

Sulphurous Oxide, SO²:

Sm (16°—202°) 1 m ³	= 0.4447 (Regnault).
1 kilo.	= 0.1544.

If we assume that the molecular specific heat of SO² is 8 Calories (from the rule that the molecular specific heat of a gas at constant pressure is 5+n, where n is the number of atoms in the molecule), we would have

$$S \text{ (at } 0^\circ) \text{ 1 m}^3 = \frac{8}{22.22} = 0.36 \text{ Cal.}$$

Combining this with Regnault's value of Sm, we would get the formula

$$\begin{aligned} \text{Sm } (0^\circ \text{ to } t^\circ) \text{ 1 m}^3 &= 0.36 + 0.0003t \\ \text{1 kilo.} &= 0.125 + 0.0001t \end{aligned}$$

These values are probably accurate enough for furnace calculations, and are very useful in pyritic smelting and the roasting of sulphide ores. While it is always desirable to have direct determinations of such important quantities, yet when they have never been made it is allowable to work out and use the most probable values.

Sulphuric Oxide, SO³:

The specific heat of this important gas has not been measured, As an approximation we may assume

$$\begin{aligned} \text{S (at } 0^\circ) \text{ per molecule} &= 9.0 \text{ Cal. (assumed).} \\ \text{per m}^3 &= 0.405 \text{ Cal.} \\ \text{per kilogram} &= 0.10 \text{ Cal.} \end{aligned}$$

For getting an approximation to Sm we may assume the coefficient of t the same as in NH³, which contains the same number of atoms and is of analogous formula, and we then have

$$\begin{aligned} \text{Sm } (0^\circ \text{ to } t^\circ) \text{ per molecule} &= 9.0 + 0.0036t \\ \text{per m}^3 &= 0.405 + 0.00017t \\ \text{per kilogram} &= 0.100 + 0.00004t \end{aligned}$$

Calcium Oxide, CaO (lime):

This important datum has not been determined, but since it is so closely analogous to MgO, an approximation may be obtained by assuming that the molecular specific heats of the two compounds are alike. That for MgO is $0.2440 \times 40 = 9.76$ Calories. That for CaO would therefore be

$$\text{Sm } (24^\circ - 100^\circ) = \frac{9.76}{56} = 0.1743$$

and assuming a usual coefficient of t; for compounds of this type:

$$\text{Sm } (0^\circ - t^\circ) = 0.1715 + 0.00007t$$

Titanic Oxide, TiO₂:

S (up to 200°)	= 0.1790 (Nilson and Pettersson).
Q (0° to 200°)	= 35.8 Cal.
Q (0° to t°) for t over 200°	= 35.8 + 0.1790 (t—200) + .000055 (t—200) ² .

Chromium Oxide, Cr₂O₃:

Sm (10°—99°)	= 0.1796 (Regnault).
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Manganese Oxides:

MnO Sm (13°—98°)	= 0.1570 (Regnault).
Mn ² O ³ Sm (15°—99°)	= 0.1620 (Oeberg).
(Manganite) Mn ² O ³ H ² O Sm (21°—52°)	= 0.1760 (Kopp).
(Pyrolusite) MnO ² Sm (17°—48°)	= 0.1590 (Kopp).

Iron Oxides, Fe₂O₃:

Sm (0°—t°)	= 0.1456 + 0.000188t (Regnault and Richards).
Fe ³ O ⁴ Sm (0°—t°)	= 0.1447 + 0.000188t (Regnault and Richards).

Nickel Oxide, NiO:

Sm (13°—98°)	= 0.1588 (Regnault)
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Copper Oxides:

Cu ² O Sm (19°—51°)	= 0.1110 (Oeberg).
CuO Sm (12°—98°)	= 0.1420 (Regnault).

Zinc Oxide, ZnO:

Sm (0°—t°) (to t = 1000°)	= 0.1212 + 0.0000315t (Richards).
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Arsenious Oxide, As₂O₃:

Sm (13°—97°)	= 0.1276 (Regnault).
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Zirconium Oxide, ZrO₂:

Sm (0°—100°)	= 0.1076 (Nilson and Pettersson).
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Columbic Oxide, Cb₂O₅

Sm (0°—t°)	= 0.1037 + 0.000070t (Krüss and Nil- son).
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Molybdic Oxide, MoO₃:

Sm (21°—52°)	= 0.1540 (Kopp).
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Tin Oxide, SnO²:

Sm (16°—98°)	= 0.0936 (Regnault).
Sm (0—t)	= 0.1050 + 0.000006t (Richards).

Antimonious Oxide, Sb²O³:

Sm (18°—100°)	= 0.0927 (Neumann).
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Tungstic Oxide, WO³:

Sm (8°—98°)	= 0.0798 (Regnault).
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Mercuric Oxide, HgO:

Sm (5°—98°)	= 0.0518 (Regnault).
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Lead Oxide, PbO:

Sm (22°—98°)	= 0.0512 (Regnault).
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Bismuth Oxide, Bi²O³:

Sm (20°—98°)	= 0.0605 (Regnault).
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Thoric Oxide, Th²O³:

Sm (0°—100°)	= 0.0548 (Nilson and Pettersson).
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For those metallic oxides whose specific heat has not been determined, an approximation to the specific heat can be found by assuming that the metallic atoms in a molecule of oxide have each a specific heat 6.4 Calories, and each atom of oxygen in an oxide molecule has an atomic specific heat of 3.6. As a rough approximation, we can further assume that the mean specific heat from 0° to t° increases 0.04 per cent. for each degree of temperature, so that the above calculated specific heat being from 0° to 100°, we can figure out S at zero and the rate of increase of S or Sm with t.

Example: What is the most probable value of the specific heat of CaO? Since molecule weight is 56, and the molecule may be assumed to have a molecular specific heat of 6.4 + 3.6 = 10.0 Calories, the mean specific heat per kilogram (0°—100°) is $10.0 \div 56 = 0.1786$. S at zero will then be $0.1786 \div 1.04 = 0.1717$, and we would have the formulæ:

$$\begin{aligned} \text{Sm} &= 0.1717 + 0.000071t \\ \text{S} &= 0.1717 + 0.000142t \\ \text{Q} &= 0.1717t + 0.000071t^2 \end{aligned}$$

Problem 13.

The Jacobs process of producing artificial emery consists in melting down impure bauxite in an electric furnace, and letting the mass cool. Assume the bauxite to be calcined before use, and to contain

	Per cent.
Alumina.....	88
Ferric oxide (Fe ² O ³).....	5
Silica (SiO ²).....	5
Titanic oxide (TiO ²).....	2

Required:

- (1) The heat necessary to just melt a metric ton of this material at 2000°.
- (2) The net electric power theoretically required.
- (3) The total electric power actually required.

Solution:

(1) Because of the presence of the impurities the alumina melts easier than it otherwise would. We can, therefore, calculate the heat in the alumina melted at 2000°, and the heat in the others melted at their proper melting points, because they absorb their latent heats of fusion at the lower temperature. Take 1000 kilos. of material.

Heat in 1 kilo. of alumina:

$$\begin{aligned}
 Q (0^\circ-2000^\circ) &= 0.2081 (2000) + 0.0000876 (2000)^2 &&= 767 \text{ Cal.} \\
 \text{L.H.F. at } 2000^\circ &= 2.1 (2000 + 273) \div 102 \text{ (mol. wt.} \\
 &\quad \text{Al}_2\text{O}_3) &&= 47 \text{ ''} \\
 &&&\text{Total} = \underline{814} \text{ ''}
 \end{aligned}$$

Heat in 1 kilo. of ferric oxide

$$\begin{aligned}
 Q (0^\circ-1600^\circ) &= 0.1447 (1600) + 0.000188 (1600)^2 \text{ (assumed)} &&= 713 \text{ ''} \\
 \text{L.H.F. at } 1600^\circ &\div 2.1 (1600 + 273) \div 160 &&= 25 \text{ ''} \\
 \text{Heat in liquid} &= (2000-1600) \times 0.59 &&= 236 \text{ ''} \\
 &&&\text{Total} = \underline{974} \text{ ''}
 \end{aligned}$$

Heat in 1 kilo. of silica:

$$\begin{aligned}
 Q (0^\circ-1900^\circ) &= 0.1833 (1900) + 0.000077 (1900)^2 &&= 626 \text{ ''} \\
 \text{L.H.F. (Voigt)} &&&= 135 \text{ ''} \\
 Q (1900^\circ-2000^\circ) \text{ liquid} &= 0.476 \times 100 &&= 48 \text{ ''} \\
 &&&\text{Total} = \underline{809} \text{ ''}
 \end{aligned}$$

Heat in 1 kilo. of titanite oxide:

$$Q (0^\circ - 2000^\circ) = 35.8 \times 0.1790 (1800) + 0.000055 (1800)^2 = 536 \text{ Cal.}$$

$$\text{L.H.F.} = 2.1T = 2.1 (2000 + 273) \div 80 = 59 \text{ "}$$

$$\text{Total} = 595 \text{ "}$$

Total heat to fuse 1000 kilos.:

Heat in alumina	880×814	= 716,320 Cal.
Heat in ferric oxide	50×974	= 48,700 "
Heat in silica	50×809	= 40,450 "
Heat in titanite oxide	20×595	= 11,900 "
	Total	= 817,370 "

(2) One kilowatt equals 859 Calories per hour.

$$\text{Kilowatt-hours absorbed by melt} = \frac{817,370}{859} = 951.5 \text{ kw-hr.}$$

(3) Assume an efficiency of 50 per cent., requires 1903 kw-hrs. If the dynamos work at 95 per cent., efficiency, the working power of the water turbine, gas engines or steam engines would be $\frac{1903}{0.95} = 2000$ kw-hrs.

Problem 14.

The ferric oxide charged into a blast furnace is reduced at 900° C. by carbonous oxide gas, CO, according to the reaction: $\text{Fe}_2\text{O}_3 + 9\text{CO} + (17.15\text{N}^2) = \text{Fe}^2 + 3\text{CO}_2 + 6\text{CO} + (17.15\text{N}^2)$.

Required:

- (1) The thermal value of the reaction at 900° .
- (2) What would be the temperature of the resulting products after the reaction had occurred?

Solution:

(1) The 6CO and 17.15N^2 occurring on both sides of the equation need not be considered. The heat value of the equation at ordinary temperatures would therefore be:

Decomposition of Fe_2O_3	= -195,600 Cal.
Decomposition of 3CO	= - 87,480 "
Formation of 3CO ₂	= +291,600 "
Thermal value of reaction	= + 8,520 "

At 900°, the value is changed as follows:

Added:

Heat in Fe ² O ³ (160 kilos.) at 900° = 160 [0.1447		
(900) + 0.000188(900) ²]		= + 45,200 Cal.
Heat in 3CO (= 66.66 m ³) at 900° = 66.66		
[0.303(900) + 0.000027(900) ²]		= + 19,640 "
Total to be added		= + 64,840 "

Subtracted:

Heat in Fe ² (112 kilos.) at 900° = 112		
× (0.218t—39)		= 17,585 "
Heat in 3CO ² (66.66 m ³) at 900° = 66.66		
[0.37(900) + 0.00022(900) ²]		= 34,080 "
Total to be subtracted		= 51,665 "
Heat of reaction at 900° = 8,520 + 64,840—		
51,665		= + 21,695 "

(2) The above heat would serve to raise the temperature of all the products, viz.: Fe², 3CO², 6CO, 17.15N² (from blast).

Their thermal capacity, 900° to t, is:

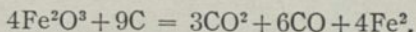
Fe ² = 112 [0.218(t—900)]	
3CO ² = 66.66 [0.37(t—900) + 0.00022(t ² —900 ²)]	
6CO = 133.33 [0.303(t—900) + 0.000027(t ² —900 ²)]	
17.15N ² = 17.15 [" "]	
Sum = 0.018517t ² + 94.68t — 100.383 = 21,695 Calories.	

Whence t = 1065°.

It follows from the preceding discussion that the reduction of iron oxide by CO, at about 900°, is an exothermic reaction, heat being evolved, and that the reaction proceeds to a finish when once started. The relations for FeO would be probably similar, but we do not have the specific heat of FeO to use in making the exact calculations.

Problem 15.

If Fe²O³ charged into a blast furnace were reduced by solid carbon, at 900° C., by the reaction



Required:

(1) The thermal value of the reaction at 900° C

(2) The temperature of the resultant products after the reaction.

Solution:

(1) Value of the reaction at zero	= - 4(195,600) Cal.
	+ 3(97,200)
	+ 6(29,160)
<i>Add:</i>	= - 315,840
Heat in 4Fe ² O ³ at 900°	= + 180,800 "
Heat in 9C at 900° = 9(12) [0.2142(900) + 0.000166(900 ²)]	= + 35,340 "
<i>Subtract:</i>	
Heat in 4Fe ² at 900°	= - 70,340 "
Heat in 3CO ² at 900°	= - 34,080 "
Heat in 6CO at 900° = 6 (22.22) [0.303 (900) + 0.000027(900 ²)]	= - 39,275 "
Algebraic sum	= - 243,395 "
Absorbed per molecule of Fe ² O ³	= - 60,850 "

This reaction is therefore strongly endothermic, and therefore tends to check itself constantly by the resultant cooling effect.

(2) If the Fe²O³ and C were at 900° to start with, the products would be below 900° after the reaction, since they would have to furnish the deficit of heat.

The products would give out in cooling from 900° to t°.

$$4\text{Fe}^2 = 4(112) [0.218(900-t)]$$

$$3\text{CO}^2 = 66.66 [0.37(900-t) + 0.00022(900^2-t^2)]$$

$$6\text{CO} = 133.33 [0.303(900-t) + 0.000027(900^2-t^2)]$$

$$\text{Sum} = 0.0183t^2 - 162.73t + 161,250, = 243,395 \text{ Cal.}$$

$$\text{Whence } t = - 537^\circ.$$

This result is, of course, due to the hypothetical assumption that this endothermic reaction would go on until completed without checking itself. The impossible result obtained means that if this single reaction really goes on, it will soon check itself on account of the decrease of temperature.

There are a few other compounds than those previously mentioned whose thermophysics has been investigated, but their number is in reality infinitesimal compared with the number of those which have not been touched. There are many

compounds of great importance in metallurgy whose specific heats are not known, to say nothing of their latent heats of fusion, etc. The wide introduction of the electric furnace has rendered desirable the latent heats of vaporization and specific heats at high temperatures, but these are altogether lacking; we can only estimate their values. It is to be hoped that many metallurgical laboratories may be incited to take up this very neglected field, and thus bring forward numerical data which would be of the greatest theoretical and practical value. One example of such work, which deserves special commendation, is the quite recent publication of Prof. J. H. L. Vogt, of Christiania, on the "Silikatschmelzlösungen," *i.e.*, on "Melted Silicate Solutions," in which determinations of the melting points and latent heats of fusion of many simple and complex silicates are given for the first time; we venture to predict that the data and conclusions of Prof. Vogt will be of great value to the physicist, chemist, metallurgist, and geologist, in both a practical as well as a theoretical sense.

In collating the remaining available data, it is rather difficult to decide as to what has immediate metallurgical interest and what has not. Electrometallurgy, in particular, is busying itself with the treatment and decomposition of so many compounds heretofore considered outside of the metallurgist's sphere of interest, that almost all of the common chemical compounds now have either a present or a prospective interest to the metallurgist.

THERMOPHYSICS OF CHLORIDES.

Hydrogen, HCl (gas):

$$\text{Sm per kilo. (22}^\circ\text{—214}^\circ) = 0.1867 \text{ (Regnault).}$$

$$\text{per m}^3 \text{ (22}^\circ\text{—214}^\circ) = 0.3067 \text{ (Regnault).}$$

Lithium, LiCl (solid):

$$\text{Sm per kilo. (13}^\circ\text{—97}^\circ) = 0.2821 \text{ Cal. (Regnault).}$$

Carbon, CCl⁴ (liquid):

$$\text{L. H. vaporization at 0}^\circ = 52.0 \text{ Cal. (Regnault).}$$

Ammonium, NH⁴Cl (solid):

$$\text{Sm per kilo. (23}^\circ\text{—100}^\circ) = 0.3908 \text{ Cal. (Neumann).}$$

Sodium, NaCl (solid):

$$\text{Sm per kilo. (15}^\circ\text{—98}^\circ) = 0.2140 \text{ Cal. (Regnault).}$$

Magnesium, MgCl^2 (solid):

Sm per kilo. (24° — 100°) = 0.1946 Cal. (Regnault).

Silicon, SiCl^4 (liquid):

Sm per kilo. (10° — 15°) = 0.1904 Cal. (Regnault).

SiCl^4 (gas) Sm per kilo.

(90° — 234°) = 0.1322 Cal. (Regnault).

SiCl^4 (gas) Sm per m^3 (90°

— 234°) = 1.0113 Cal. (Regnault).

Potassium, KCl (solid):

Sm per kilo. (14° — 99°) = 0.1730 Cal. (Regnault).

Calcium, CaCl^2 (solid):

Sm per kilo. (23° — 99°) = 0.1642 Cal. (Regnault).

Titanium, TiCl^4 (solid):

Sm per kilo. (13° — 99°) = 0.1881 Cal. (Regnault).

TiCl^4 (gas) Sm per kilo.

(163° — 271°): = 0.1290 Cal. (Regnault).

Chromium, CrCl^2 (solid):

Sm per kilo. (?) = 0.1430 Cal. (Kopp).

Manganese, MnCl^2 (solid):

Sm per kilo. = 0.1425 Cal. (Regnault).

L.H. vaporization = 49.37 Cal. (Ogier).

Copper, CuCl (solid):

Sm per kilo. (17° — 98°) = 0.1383 Cal. (Regnault).

Zinc, ZnCl^2 (solid):

Sm per kilo. (21° — 99°) = 0.1362 Cal. (Regnault).

Arsenic, AsCl^3 (solid):

Sm per kilo. (14° — $98^\circ.3$) = 0.0896 Cal. (Regnault).

(gas) Sm per kilo. (159°

— 268°) = 0.1122 Cal. (Regnault).

L.H. vaporization = 69.74 Cal. (Regnault).

Strontium, SrCl^2 (solid):

Sm per kilo. (13° — 98°) = 0.1199 Cal. (Regnault).

Silver, AgCl (solid):

Sm per kilo. (15° — 98°) = 0.0911 Cal. (Regnault).

(160° — 380°) = 0.0978 Cal. (Ehrhardt).

Tin(ous), SnCl^2 (solid):

Sm per kilo. (20° — 99°) = 0.1016 Cal. (Regnault).

Tin(ic), SnCl^3 (liquid):

Sm per kilo. (14° — 98°) = 0.1476 Cal. (Regnault).

(gas) Sm per kilo. (149°

— 273°) = 0.0939 Cal. (Regnault).

L.H. vaporization at 112° = 46.84 Cal. (Regnault).

Barium, BaCl^2 (solid):

Sm per kilo. (14° — 98°) = 0.0896 Cal. (Regnault).

Mercurous, HgCl (solid):

Sm per kilo. (7° — 99°) = 0.0521 Cal. (Regnault).

Mercuric, HgCl^2 (solid):

Sm per kilo. (13° — 98°) = 0.0689 Cal. (Regnault).

Lead, PbCl^2 (solid):

Sm per kilo. (20° — 100°) = 0.0651 Cal. (Luginin).

(160° — 380°) = 0.0707 Cal. (Ehrhardt).

(liquid) Sm per kilo. above

485° = 0.1035 Cal. (Ehrhardt).

L.H. fusion at 485° = 20.90 Cal. (Ehrhardt).

THERMOPHYSICS OF BROMIDES.

Hydrogen, HBr (gas):

Sm per kilo. (11° — 100°) = 0.0820 Cal. (Strecker).

Sm per m^3 (11° — 100°) = 0.2989 Cal. (Strecker).

Sodium, NaBr :

Sm per kilo. (?) = 0.1384 Cal. (Regnault).

Potassium, KBr (solid):

Sm per kilo. (16° — 98°) = 0.1132 Cal. (Regnault).

Silver, AgBr (solid):

Sm per kilo. (15° — 98°) = 0.0739 Cal. (Regnault).

Lead, PbBr^2 (solid):

Sm per kilo. (16° — 98°) = 0.0532 Cal. (Regnault).

(190° — 430°) = 0.0532 Cal. (Ehrhardt).

L.H. fusion at 490° = 12.34 Cal. (Ehrhardt).

THERMOPHYSICS OF IODIDES.

Hydrogen, HI (gas):

Sm per kilo. (21° — 100°) = 0.0550 Cal. (Strecker).

Sm per m^3 (21° — 100°) = 0.3168 Cal. (Strecker).

Sodium, NaI (solid):

Sm per kilo. (16°—99°) = 0.0868 Cal. (Regnault).

Potassium, KI (solid):

Sm per kilo. (20°—99°) = 0.0819 Cal. (Regnault).

Cuprous, CuI (solid):

Sm per kilo. (18°—99°) = 0.0687 Cal. (Regnault).

Silver, AgI (solid):

Sm per kilo (15°—264°) = 0.0577 Cal. (Bellati and Romanese).

Mercurous, HgI (solid):

Sm per kilo. (17°—99°) = 0.0395 Cal. (Regnault).

Mercuric, HgI² (solid):

Sm per kilo. (18°—99°) = 0.0420 Cal. (Regnault).

Lead, PbI² (solid):

Sm per kilo. (14°—98°) = 0.0427 Cal. (Regnault).

(160°—315°) = 0.0430 Cal. (Ehrhardt).

(liquid) above 375° = 0.0645 Cal. (Ehrhardt).

L.H. fusion at 375° = 11.50 Cal. (Ehrhardt).

THERMOPHYSICS OF FLUORIDES.

Sodium-Aluminium, 3NaF, AlF³:

Sm per kilo. (16°—99°) = 0.2522 (Oeberg).

(Cryolite)

Calcium (Fluorspar), CaF²:

Sm per kilo. (15°—99°) = 0.2154 (Regnault).

THERMOPHYSICS OF SULPHATES.

Hydrogen, H²SO⁴:

Sm per kilo. (5°—22°) = 0.332 (Cattanes).

L.H. vaporization at 326° = 122.1 Cal. (Person).

Sodium, Na²SO⁴:

Sm per kilo. (17°—98°) = 0.2312 (Regnault).

Magnesium, MgSO⁴:

Sm per kilo. (25°—100°) = 0.2250 (Pape).

Potassium, K²SO⁴:

Sm per kilo. (15°—98°) = 0.1901 (Regnault).

KHSO⁴:

Sm per kilo. (19°—51°) = 0.2440 (Kopp).

Calcium, CaSO⁴:

Sm per kilo. (13°—98°) = 0.1965 (Regnault).

Manganese, MnSO⁴:

Sm per kilo. (21°—100°) = 0.1820 (Pape).

Nickel, NiSO⁴:

Sm per kilo. (15°—100°) = 0.2160 (Pape).

Copper, CuSO⁴:

Sm per kilo. (23°—100°) = 0.1840 (Pape).

Zinc, ZnSO⁴:

Sm per kilo. (22°—100°) = 0.1740 (Pape).

Strontium, SrSO⁴:

Sm per kilo. (22°—99°) = 0.1428 (Regnault).

Barium, BaSO⁴:

Sm per kilo. (10°—98°) = 0.1128 (Regnault).

Lead, PbSO⁴:

Sm per kilo (20°—99°) = 0.0827 (Regnault).

THERMOPHYSICS OF NITRATES.

Hydrogen, HNO³:

L.H. vaporization at 326° = 115.1 Cal. (Person).

Ammonium, NH⁴NO³:

Sm per kilo. (14°—31°) = 0.4550 (Kopp).

Sodium, NaNO³:

Sm per kilo. (14°—98°) = 0.2782 (Regnault).

NaNO³ (fluid) Sm per kilo
(320°—430°) = 0.4130 (Person).NaNO³ L.H. fusion at
305.5° = 64.87 Cal. (Person).*Potassium, KNO³:*

Sm per kilo. (13°—98°) = 0.2387 (Regnault).

KNO³ (fluid) Sm per kilo.
(350°—435°) = 0.3319 (Person).KNO³ L.H. fusion at 333.5° = 48.90 Cal. (Person).*Sodium-potassium, (K,Na)NO³:*

Sm per kilo. (15°—100°) = 0.2350 (Person).

Strontium, Sr(NO³)²:

Sm per kilo. (17°—47°) = 0.1810 (Kopp).

Silver, AgNO^3 :

Sm per kilo. (16° — 99°) = 0.1435 (Regnault).

Barium, $\text{Ba(NO}^3)^2$:

Sm per kilo. (13° — 98°) = 0.1523 (Regnault).

Lead, $\text{Pb(NO}^3)^2$:

Sm per kilo. (17° — 100°) = 0.1173 (Neumann).

THERMOPHYSICS OF CARBONATES.

Sodium, Na^2CO^3 :

Sm per kilo. (16° — 98°) = 0.2728 (Regnault).

Potassium, K^2CO^3 :

Sm per kilo. (23° — 99°) = 0.2162 (Regnault).

Calcium (calcite), CaCO^3 :

Sm per kilo. (20° — 100°) = 0.2086 (Regnault).

Calcium (aragonite), CaCO^3 :

Sm per kilo. (18° — 99°) = 0.2085 (Regnault).

Calcium (marble), CaCO^3 :

Sm per kilo. (23° — 98°) = 0.2099 (Regnault).

Calcium-magnesium, $\text{CaMg(CO}^3)^2$:

Sm per kilo. (20° — 100°) = 0.2179 (Regnault).

Magnesium-iron, $\text{Mg}^7\text{Fe}^2(\text{CO}^3)^9$:

Sm per kilo. (17° — 100°) = 0.2270 (Neumann).

Iron (siderite), FeCO^3 :

Sm per kilo. (9° — 98°) = 0.1935 (Regnault).

Strontium, SrCO^3 :

Sm per kilo. (8° — 98°) = 0.1475 (Regnault).

Barium, BaCO^3 :

Sm per kilo. (11° — 99°) = 0.1104 (Regnault).

Lead (cerussite), PbCO^3 :

Sm per kilo. (16° — 47°) = 0.0791 (Kopp).

THERMOPHYSICS OF CHROMATES.

Potassium, K^2CrO^4 :

Sm per kilo. (19° — 98°) = 0.1851 (Regnault).

Potassium, $\text{K}^2\text{Cr}^2\text{O}^7$:

Sm per kilo. (16° — 98°) = 0.1894 (Regnault).

Lead, PbCrO_4 :

Sm per kilo. (19° — 50°) = 0.0900 (Kopp).

(Chromite), FeCrO_4 :

Sm per kilo. (19° — 50°) = 0.1590 (Kopp).

THERMOPHYSICS OF BORATES.

Sodium, $\text{Na}_2\text{B}_2\text{O}_4$:

Sm per kilo. (17° — 97°) = 0.2571 (Regnault).

$\text{Na}_2\text{B}_4\text{O}_7$:

Sm per kilo. (16° — 98°) = 0.2382 (Regnault).

Potassium, $\text{K}_2\text{B}_2\text{O}_4$:

Sm per kilo. (16° — 98°) = 0.2048 (Regnault).

$\text{K}_2\text{B}_4\text{O}_7$ Sm per kilo. (18°

— 99°) = 0.2198 (Regnault).

Lead, PbB_2O_4 :

Sm per kilo. (15° — 98°) = 0.0905 (Regnault).

PbB_4O_7 Sm per kilo. (16°

— 98°) = 0.1141 (Regnault).

THERMOPHYSICS OF PHOSPHATES.

Sodium, $\text{Na}_4\text{P}_2\text{O}_7$:

Sm per kilo. (17° — 98°) = 0.2283 (Regnault).

Potassium, $\text{K}_4\text{P}_2\text{O}_7$:

Sm per kilo. (17° — 98°) = 0.1901 (Regnault).

Calcium, CaP_2O_6 :

Sm per kilo. (15° — 98°) = 0.1992 (Regnault).

(Apatite), $3\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{CaF}_2$:

Sm per kilo. (15° — 99°) = 0.1903 (Oeberg).

Silver, Ag_3PO_4 :

Sm per kilo. (19° — 50°) = 0.0898 (Kopp).

Lead, $\text{Pb}_2\text{P}_2\text{O}_7$:

Sm per kilo. (11° — 98°) = 0.0821 (Regnault).

Lead, $\text{Pb}_3\text{P}_2\text{O}_8$:

Sm per kilo. (11° — 98°) = 0.0798 (Regnault).

THERMOPHYSICS OF ALUMINATES, ETC.

Spinel, MgAl_2O_4 :

Sm per kilo. (15° — 47°) = 0.1940 (Kopp).

Chrysoberyl, BeAl_2O_4 :

Sm per kilo. (0° — 100°) = 0.2004 (Nilson and Petterson).

Ilmenite, FeTiO_3 :

Sm per kilo. (15° — 50°) = 0.177 (Kopp).

Wulfenite, PbMoO_4 :

Sm per kilo. (15° — 50°) = 0.083 (Kopp).

Scheelite, CaWO_4 :

Sm per kilo. (15° — 50°) = 0.097 (Kopp).

Wolframite, Fe(Mn)WO_4 :

Sm per kilo. (15° — 50°) = 0.098 (Kopp).

KMnO_4 Sm per kilo. (15°

— 50°) = 0.179 (Kopp).

KClO_3 Sm per kilo. (10°

— 100°) = 0.210 (Regnault).

MISCELLANEOUS.

Glass, Ca, K Silicate:

Sm per kilo. (14° — 99°) = 0.1977 (Regnault).

Sm per kilo. (0° — 300°) = 0.190 (Dulong and Petit).

Flint Glass:

Sm per kilo. (10° — 50°) = 0.117 (H. Meyer).

Crown Glass:

Sm per kilo. (10° — 50°) = 0.161 (H. Meyer).

Paraffin (solid):

Sm per kilo. (10° — 15°) = 0.562 (Battelli).

Sm per kilo. (35° — 40°) = 0.622 (Battelli).

(fluid) Sm per kilo. (52°

— 63°) = 0.706 (Battelli).

Beeswax (solid):

Sm per kilo. (26° — 42°) = 0.820 (Person).

Sm per kilo. (42° — 58°) = 1.720 (Person).

(fluid) Sm per kilo. (65°

— 100°) = 0.499 (Person).

Vulcanite:

Sm per kilo. (20° — 100°) = 0.331 (A. M. Mayer).

Soft Para Rubber:

Sm per kilo. (0° — 100°) = 0.481 (H. Gee and Terry).

Ammonia gas, NH_3

Sm (o-t) 1 m^3 = $0.38 + 0.00016t$ (Le Chatelier).

Methane, CH_4

Sm (o-t) 1 m^3 = $0.38 + 0.00022t$

Ethelyne, C_2H_4

Sm (o-t) 1 m^3 = $0.46 + 0.0003t$ (Le Chatelier).

THERMOPHYSICS OF SULPHIDES.

Hydrogen, H²S (gas):

Sm per kilo. (20°—206°) = 0.2451 (Regnault).

Sm per m³ (20°—206°) = 0.3750 Cal. (Regnault).(0—t) 1m³ = 0.34 + 0.00015t.*Carbon, CS² (liquid):*

Sm per kilo. (14°—29°) = 0.2468 (Person).

(gas) Sm per kilo. (86°—

190°) = 0.1596 (Regnault).

Sm per m³ (86°—190°) = 0.5458 (Regnault).

L.H. vaporization at 46° = 83.8 Cal. (Wirtz).

Manganese, MnS:

Sm per kilo. (10°—100°) = 0.1392 (Sella).

Iron, FeS:

Sm per kilo. (17°—98°) = 0.1357 (Regnault).

(Pyrrhotite), Fe⁷S⁸:

Sm per kilo. (20°—100°) = 0.1602 (Regnault).

(Pyrites), FeS²:

Sm per kilo. (19°—98°) = 0.1301 (Regnault).

Decomposed, giving off S, at 565° (L. U. Laboratory).

Nickel, NiS:

Sm per kilo. (15°—98°) = 0.1281 (Regnault).

Cobalt, CoS:

Sm per kilo. (15°—98°) = 0.1251 (Regnault).

Copper, Cu²S:

Sm per kilo. (9°—97°) = 0.1212 (Regnault).

Sm per kilo. (0°—t°) = 0.1126 + 0.00009t (Bellati and Lussana).

Zinc, ZnS:

Sm per kilo. (15°—98°) = 0.1230 (Regnault).

Arsenic, AsS:

Sm per kilo. (20°—100°) = 0.1111 (Neumann).

As²S³ Sm per kilo. (20°—

100°) = 0.1132 (Naumann).

(0—t) 1 m³ = 0.34 + 0.00015t*Molybdenum, MoS²:*

Sm per kilo. (20°—100°) = 0.1233 (Regnault).

Silver, Ag²S:

Sm per kilo. (7°—98°) = 0.0746 (Regnault and Sella).

Sm per kilo. (0°—t°) = 0.0685 + 0.00005t (Bellati and Lussana).

Tin, SnS:

Sm per kilo. (13°—98°) = 0.0837 (Regnault).

SnS² Sm per kilo. (12°—
95°) = 0.1193 (Regnault).

Antimony, Sb²S³:

Sm per kilo. (23°—99°) = 0.0840 (Regnault).

Mercury, HgS:

Sm per kilo. (14°—98°) = 0.0512 (Regnault).

Lead, PbS:

Sm per kilo. (16°—98°) = 0.0509 (Regnault).

Q (melted, at 1050°) = 104 Cal. (L. U. Laboratory).

Bismuth, Bi²S³:

Sm per kilo. (11°—99°) = 0.0600 (Regnault).

THERMOPHYSICS OF COMPOUND SULPHIDES.

Bornite, Cu³FeS³:

Sm per kilo. (10°—100°) = 0.1177 (Sella).

Chalcopyrite, CuFeS² :

Sm per kilo. (14°—98°) = 0.1310 (Kopp).

Decomposed, giving off S, at 720° (L. U. Laboratory).

Tetrahedrite, Cu⁴Sb²S⁷:

Sm per kilo. (10°—100°) = 0.0987 (Sella).

Bournonite, PbCuSbS³:

Sm per kilo. (10°—100°) = 0.0730 (Sella).

Mispickel, FeAsS:

Sm per kilo. (10°—100°) = 0.1030 (Sella).

Cobaltite, CoAsS:

Sm per kilo. (15°—99°) = 0.0991 (Sella).

Proustite, Ag³AsS³:

Sm per kilo. (10°—100°) = 0.0807 (Sella).

Pyrargyrite, Ag³SbS³:

Sm per kilo. (10°—100°) = 0.0757 (Sella).

THERMOPHYSICS OF ARSENIDES AND ANTIMONIDES.

Löllingite, FeAs²:

Sm per kilo. (10°—100°) = 0.864 (Sella).

Smaltite, CoAs²:

Sm per kilo. (10°—100°) = 0.0830 (Sella).

Domeykite, Cu^3As :

Sm per kilo. (10° — 100°) = 0.0949 (Sella).

Dyscrasite, Ag^3Sb :

Sm per kilo. (10° — 100°) = 0.0558 (Sella).

THERMOPHYSICS OF SILICATES.

Magnesium (Olivin), Mg^2SiO^4 :

Sm (100° — 0°) = 0.2200 (Vogt).

Melting point = 1400° (Vogt).

L. H. fusion = 130 Cal. (Vogt).

Q (solid) (0° — 1400°) = 520 Cal. (Vogt).

Magnesium (Enstatite), MgSiO^3 (with a little Ca replacing Mg):

Sm (0° — 100°) = 0.206 (Vogt).

Sm (0° — 1200°) = 0.301 (Vogt).

Melting point = 1300° (Vogt).

Q (solid) (0° — 1300°) = 403 Cal. (Vogt).

L. H. fusion = 125 Cal. (Vogt).

Aluminium (Topaz), $\text{Al}^2\text{Si}(\text{F})\text{O}^5$:

Sm (12° — 100°) = 0.1997 (Joly).

Aluminium-Beryllium (Beryl), $\text{BeAl}^2\text{Si}^2\text{O}^8$:

Sm (12° — 100°) = 0.2066 (Joly).

Potassium-Aluminium (Microcline), KAlSi^3O^8 —Triclinic

Sm (20° — 100°) = 0.197 (Bogajawlensky).

Melting point = 1170° (Vogt).

L. H. fusion = 83 Cal. (Vogt).

Potassium-Aluminium (Orthoclase) KAlSi^3O^8 —Monoclinic:

Sm (20° — 100°) = 0.1877 (Oeberg).

Melting point = 1200° (Vogt).

L. H. fusion = 100 Cal. (Vogt).

Calcium-Aluminium (Anorthite), $\text{CaAl}^2\text{Si}^2\text{O}^8$:

Sm (100° — 0°) = 0.189 (Vogt).

Sm (1200° — 0°) = 0.294 (Vogt).

Melting point = 1220° (Vogt).

Q (solid) (0° — 1220°) = 358 Cal. (Vogt).

L. H. fusion = 100 Cal. (Vogt).

Calcium (Wollastonite), CaSiO^3 :

Sm (0° — 100°) = 0.179 (Vogt).

Sm (0° — 1200°) = 0.288 (Vogt).

Melting point = 1250° (Vogt).

Q (solid) (0°—1250°)	= 360 Cal. (Vogt).
L. H. fusion	= 100 Cal. (Vogt).
<i>Calcium-Magnesium</i> (Malacolite), $\text{Ca}^3\text{MgSi}^4\text{O}^{12}$:	
Sm (0°—100°)	= 0.186 (Vogt).
Sm (0°—1200°)	= 0.264 (Vogt).
Melting point	= 1200° (Vogt).
Q (solid) (0°—1200°)	= 319 Cal. (Vogt).
L. H. fusion	= 94 Cal. (Vogt).
<i>Calcium-Magnesium</i> (Diopside), $\text{CaMgSi}^2\text{O}^6$:	
Sm (0°—100°)	= 0.194 (Vogt).
Sm (0°—1200°)	= 0.281 (Vogt).
Melting point	= 1225° (Vogt).
Q (solid) (0°—1225°)	= 344 Cal. (Vogt).
L. H. fusion	= 100 Cal. (Vogt).
<i>Iron</i> (Fayalite), Fe^2SiO^4 :	
Sm (0°—100°)	= 0.1700 (Vogt).
Q (solid) (0°—1040°)	= 310 Cal. (Vogt).
L. H. fusion	= 85 Cal. (Vogt).
<i>Iron-Aluminium</i> (Garnet), $\text{Fe}^3\text{Al}^2\text{Si}^3\text{O}^{12}$:	
Sm (16°—100°)	= 0.1758 (Oeberg).
Melting point	= 1145° (Joly).
<i>Zirconium</i> (Zircon), ZrSiO^4 :	
Sm. (15°—100°)	= 0.1456 (Regnault).
Melting point	= 1760° (Joly).
(Pumice) Sm (10°—100°)	= 0.240 (Dunn).
(Lava from Etna, 1669).	
Sm (0°—500°)	= 0.182 + 0.000155t (Bartoli).
Sm (500°—800°)	= 0.270 (Bartoli).
(Crystalline Slag).	
Sm (14°—99°)	= 0.1888 (Oeberg).
(Enamel Slag.)	
Sm (15°—99°)	= 0.1865 (Oeberg).
(Bessemer Slag.)	
Sm. (14°—99°)	= 0.1691 (Oeberg).
(Basalt) Sm (20°—470°)	= 0.1990 (Roberts Austen).
(Granite) Sm (20°—524°)	= 0.2290 (Bartoli).

For silicates in general, the specific heat is found to agree fairly well with what would be calculated from their percent-

age composition, giving each oxide constituent its proper specific heat. Those oxides whose specific heat at 0° are known are as follows:

SiO^2	= 0.1833 (Richards)
Al^2O^3	= 0.2081 (Richards).
Fe^2O^3	= 0.1456 (Richards).
MgO	= 0.2420 (Regnault).
CaO	= 0.1779 (calculated).

Those which are not known give good results if assumed to be as follows:

FeO	= 0.1460 (Vogt).
MnO	= 0.1511 (Vogt).
K^2O	= 0.1390 (Vogt).
Na^2O	= 0.2250 (Vogt).
Li^2O	= 0.4430 (Vogt).

Using these data, S at 0° is calculated from the percentage composition of the silicate. For S at higher temperatures it can be assumed with considerable approximation to the truth, that S increases 0.078 per cent. for each degree, and so, calling S_0 the specific heat at zero, we would have

$$\begin{aligned} S &= S_0 (1 + 0.00078t) \\ S_m &= S_0 (1 + 0.00039t) \\ Q (0^\circ - t^\circ) &= S_m \times t \end{aligned}$$

Besides the above generalizations, which enable one to calculate the heat in the solid silicate at the melting point (when the latter is known), Vogt has shown that if the heat necessary to heat the silicate from -273° to the melting point is calculated, the latent heat of fusion may be taken as being 20 to 25 per cent. of this quantity, say an average of 22.5 per cent. and thus the heat required for fusion may be approximately calculated.

Akerman has determined for many metallurgical silicate slags the total heat contained per kilogram of melted slag at the melting point. These quantities vary from 347 to 530 Calories, depending principally on the elevation of the melting point of the slag. A brief tabulation of Akerman's results are as follows, arranged according to the amount of heat in the just-melted slag:

Calories.	%SiO ²	%CaO	%Al ² O ³
347.....	{ 59	36	5
	{ 39	42	19
350.....	{ 63	35	2
	{ 58	35	7
	{ 58	37	5
	{ 53	37	10
	{ 41	42	17
	{ 38	47	15
	{ 39	43	19
360.....	{ 37	40	23
	{ 66	32	2
	{ 59	38	3
	{ 48	42	10
	{ 40	48	12
	{ 34	48	18
	{ 31	37	32
380.....	{ 46	37	17
	{ 58	32	10
	{ 58	27	15
	{ 62	37	1
	{ 38	52	10
400.....	{ 25	34	41
	{ 44	33	23
	{ 60	20	20
	{ 65	35	0
	{ 41	52	7
	{ 37	53	10
	{ 21	32	47
	{ 43	30	27

The above includes most varieties of acid and basic iron blast-furnace slags. Data for other slags made in the metallurgy of iron and of other metals, are almost altogether lacking. A wide field is here open for metallurgical experiments; data thus obtained would be immediately useful in practical calculations.

CHAPTER VI.

ARTIFICIAL FURNACE GAS.

There are many different forms of producers for making artificial furnace gas. For the purposes of making calculations upon them they may be conveniently divided into four classes, as follows:

1. Simple producers, those which use ordinary fuels, such as wood, peat, lignite, bituminous coal or anthracite, and in which no water or water vapor is introduced other than the water in the fuel itself and the normal moisture of the air used.

2. Mixed gas producers, in which water vapor or steam is introduced with the air for combustion, in such amount as to be entirely decomposed in passing through the fuel.

3. Mond gas producers, in which, for a special purpose, more steam is introduced than can be decomposed in the producer, thus producing very wet gas.

4. Water gas producers, in which air and steam alone are alternately fed to the producer, the former for heating up, the latter for producing water gas.

As far as the calculations are concerned, the essential difference between these classes is the varying amount of water vapor or steam introduced under the fuel bed while producing the gas, from all air in Class 1 to all steam in Class 4.

The calculations which it is of immediate interest to make, and the results of which are of immediate value to the metallurgist, are those concerned with the volume of gas produced per unit of fuel, its calorific power compared to that of the fuel from which it is produced, the items of the heat losses during the operation of transforming the solid fuel into gaseous fuel, the function of steam in the producer, the limits up to which the use of steam is permissible, the increase of efficiency of the gas by subsequently drying it, the advantages as to final efficiency which are gained by gasifying the fuel over burning solid fuel directly.

For information as to the construction and operation of gas producers, reference may be made to treatises such as Sexton's or Wyer's "Producer Gas," Groves and Thorp's "Chemical Technology, Vol. V., Fuels." Trade pamphlets and catalogues, such as those of R. D. Wood and Co. on "Gas Producers," of the De la Vergne Machine Co. on "Koerting Gas Engines and Gas Producers," etc., contain a great deal of exact and useful information, and may be usually had for the asking. The monograph of Jüptner and Toldt on "Generatoren und Martinöfen" (Felix, Leipzig, 1900), is concerned wholly with calorimetric calculations concerning the production of gas and its utilization in regenerative gas furnaces.

1.—SIMPLE PRODUCERS.

In these a deep bed of fuel is burnt by air or fan blast, introducing no more moisture than happens to be in the atmosphere at the time being. The fuel fed into the producer is first dried by the hot gases, then is heated and distilled or coked, and finally is oxidized by the incoming air. The residue is the ash of the coal, which is ground out at the bottom or drops through the grate, containing more or less unburnt fixed carbon. Great loss of efficiency sometimes occurs from the ashes being rich in carbon. The escaping gases issue at temperatures of 300° up to 1000° C., carrying much sensible heat out of the producer.

Calculations as to the amount of gas produced per unit of fuel consumed are to be based entirely on the carbon. The gas must be carefully analyzed, so that it can be calculated from this analysis how much carbon, in weight, is contained in a given volume of gas. (An alternative method is to take a carefully measured volume of the gas, mix it with excess of oxygen, and explode in a gas burette, determining the amount of carbon dioxide formed, and from that calculate the weight of carbon in the volume of gas taken.) Knowing this, the rest is simple; the carbon in unit weight of fuel minus the carbon lost in the ashes by poor combustion gives the weight of carbon gasified; this divided by the weight of carbon in unit volume of gas produced, gives the volume of the latter per unit weight of fuel.

Illustration: A fuel used in a gas producer contains 12 per

cent. of *ash* and 72 per cent. of carbon. The *ashes* made contain 20 per cent. of unburnt carbon; the gas produced contains by analysis and calculation 0.162 ounce of carbon per cubic foot of gas, measured at 60° F. and 29.8 inches barometric pressure. What volume of gas, measured at above conditions, is being produced per ton of 2240 pounds of coal used?

Solution: The distinction between *ash* and *ashes* must be noted; the former is the analytical expression for the amount of inorganic material left after complete combustion during the chemical analysis; the latter term means the waste matter produced industrially, and consists, if weighed dry, of the true ash, plus any unburnt carbon. The calculations are therefore as follows:

	Lbs.
Ash in 2240 pounds of coal = 2240×0.12	= 268.8
Ashes corresponding = $268.8 \div 0.80$	= 336.0
(the ashes are 80 per cent. ash)	
Carbon in the ashes	= 67.2
Carbon in the coal = 2240×0.72	= 1612.8
Carbon going into the gas (gasified)	= 1545.6
Carbon in 1 cubic foot of gas = $0.162 \div 16$	= 0.010125
Volume of gas produced per 2240 pounds of coal = $1545.6 \div 0.010125$	= 152,652 cu. ft

It will be noted that these calculations absolutely require the percentage of *total* carbon in the fuel, as determined by chemical analysis. This is not a difficult analysis, as it consists in burning the carbon in a heated tube in a stream of oxygen or air free from carbon dioxide; the products of combustion are dried and then passed through caustic potash solution to absorb CO_2 gas, the weight of which is obtained by the increased weight of the potash bulb, and the total carbon thus obtained. The fixed carbon and volatile matter of the coal, as determined by the ordinary proximate analysis, cannot be used in this calculation, since while all the fixed carbon is carbon, the volatile matter is of variable composition, containing such varying proportions of carbon that no fixed percentage of the latter in it can be assumed without considerable possible error.

The calorific power of the gas, per cubic meter or cubic foot, can be calculated from its analysis, using the calorific powers of the combustible constituents as already given in our

tables. This, multiplied by the volume of gas produced per unit of coal, gives the calorific power of the gas as compared with that of the coal from which it is made. The difference is the heat loss in the operation of producing the gas, including loss by unburnt carbon in the ashes. In fact, we may state that the heat balance is based on the following equations:

$$\begin{aligned} & \text{Heating power of the coal, per unit} \\ - & \text{Heating power of the gas per unit of coal} \\ = & \text{Calorific losses in conversion.} \end{aligned}$$

The latter item is composed of:

- Loss by unburnt carbon in the ashes.
- Sensible heat of the hot gases issuing.
- Heat conducted to the ground.
- Heat radiated to the air.

These items may be modified as follows: If the air used is hotter than the normal outside temperature, its sensible heat above this datum should be added to the heating power of the coal, because it increases the total available heat. If the ashes are removed hot, and not allowed to be completely cooled by the incoming air, their sensible heat should be included in the calorific losses during conversion. If the air used is moist, its moisture will be decomposed to hydrogen and oxygen, but the heat absorbed in doing this is exactly represented by the calorific power of this increased amount of hydrogen in the gases, and the heat absorbed is not lost but really represents so much saved as available calorific power of the gases. This item must, therefore, *not* be counted as one of the heat losses during the operation, as those losses have been defined by us. If the fuel is wet, considerable heat is required to evaporate the moisture in it, but this heat is *not* to be reckoned as one of the losses in conversion, if we have taken as the heating power of the coal the practical metallurgical value; that is, its value assuming all the water in its products of combustion to remain as vapor and none to condense. If this value has been so taken, the heat required to vaporize the moisture in the coal will have already been allowed for. Similarly, it may take a little heat energy to break up a bituminous coal so as to expel its volatile matter, but this should not be reckoned in as

a heat loss in the producer, because a little reflection will show that, whatever this amount may be, it has been properly allowed for in the determination or calculation of the total calorific power of the fuel. Jüptner and Toldt call this the "gasifying heat," and use it in all their calculations, but it is doubtful whether it really amounts to an appreciable quantity, for one thing, and even if it does it should not be reckoned as a heat loss in the producer.

Problem 16.

Jüptner and Toldt ran a gas producer with lignite of the following composition: (*Generatoren*, p. 49).

Carbon.....	69.83	per cent.
Hydrogen.....	4.33	"
Nitrogen.....	0.50	"
Oxygen.....	12.38	"
Moisture.....	7.25	"
Ash.....	5.71	"

Of this coal, 3214 kilograms was used in 8 hours, 50 minutes, producing gas which contained, analyzed dry, by volume:

Carbon dioxide, CO ²	5.21	per cent.
Carbon monoxide, CO.....	23.99	"
Oxygen, O ²	0.63	"
Methane, CH ⁴	0.25	"
Hydrogen, H ²	10.64	"
Nitrogen, N ²	59.28	"

The ashes produced weighed 22.23 kilograms per 100 kilograms of coal used, and contained 68.76 per cent. of unburned carbon. The calorific power of the coal, determined in the calorimetric bomb (in compressed oxygen, moisture resulting condensed) was 6949 Calories per gramme. Temperature of hot gases, 282° C.; temperature of air used, 9° C.; humidity, 76 per cent.; barometer, 712 millimeters of mercury.

Required:

1. The volume of gas, measured at 0° and 760 mm. pressure (and assumed dry), produced per metric ton (1000 kilos. = 2204 pounds) of fuel used.

2. The calorific power of the coal, per kilogram, with moisture formed by its combustion assumed uncondensed.
3. The proportion of the calorific power of the coal developable by burning the gas produced from it.
4. The loss of heat in conversion.
5. The loss of heat by unburnt carbon in the ashes.
6. The loss of heat as sensible heat in the gases.
7. The loss of heat by radiation and conduction, expressed:
 - (a) Per unit of coal burnt.
 - (b) Per minute.
8. The volume of air required by the producer, at the conditions of the atmosphere, per kilogram of coal burnt.

Solution:

- (1) The gas contains, per cubic meter at standard conditions:

Carbon in CO^2 0.0521×0.54 kilos.

Carbon in CO 0.2399×0.54 “

Carbon in CH^4 0.0025×0.54 “

Total $0.2946 \times 0.54 = 0.1590$ kilos.

The carbon gasified from 1000 kilograms of coal is:

Carbon in coal = 698.3 kilos.

Carbon in ashes $222.3 \times 0.6876 = 152.8$ “

Carbon gasified = 545.5 “

Therefore,

$$\text{Gas (dry) produced} = \frac{545.5}{0.1590} = 3430 \text{ cubic meters. (1)}$$

- (2) The calorific power of the coal as given must be diminished by the heat required to vaporize all the moisture formed by its combustion, leaving such moisture as theoretical moisture at 0°C . There will be formed per kilogram of coal:

From moisture of coal = 0.0725 kilos.

From hydrogen $0.0433 \times 9 = 0.3897$ “

Total = 0.4622 “

To evaporate this to theoretical moisture at zero (thus

putting the water vapor on the same footing as the other products of combustion, CO^2 and N^2) requires:

$$0.4622 \times 606.5 \text{ (Regnault),} = 280 \text{ Calories,}$$

leaving as the metallurgical or practical calorific power

$$6949 - 280 = 6669 \text{ Calories,} \quad (2)$$

(3) The calorific power of each cubic meter of gas (measured dry at standard conditions) is

$$\text{CO} = 0.2399 \text{ m}^3 \times 3,062 = 734.6 \text{ Calories}$$

$$\text{CH}^4 = 0.0025 \text{ m}^3 \times 8,598 = 21.5 \quad "$$

$$\text{H}^2 = 0.1064 \text{ m}^3 \times 2,613 = 278.0 \quad "$$

$$\text{Total} = \underline{1034.1} \quad "$$

Calorific power of gas from 1 kilogram of coal:

$$1034.1 \times 3.43 = 3547.0 \text{ Calories.}$$

$$\text{which equals } \frac{3547.0}{6669.0} = 53.2 \text{ per cent.} \quad (3)$$

(4) The loss of calorific power in conversion is $100 - 53.2 = 46.8$ per cent. of the calorific power of the coal, or per kilogram of coal:

$$6669 - 3547 = 3122 \text{ Calories.} \quad (4)$$

(5)

$$\text{Carbon in ashes} = 0.1528 \times 8100 = 1237.7 \text{ Cal.}$$

$$= 18.6 \text{ per cent.} \quad (5)$$

(6) The gases produced carry off, per cubic meter measured dry, the following amounts of heat:

Volume \times mean specific heat ($0^\circ - 282^\circ$) = heat capacity per 1° .

$$\text{CO}^2 \quad 0.0521 \times 0.432 = 0.0225$$

$$\text{CH}^4 \quad 0.0025 \times 0.428 = 0.0011$$

$$\left. \begin{array}{l} \text{CO} \\ \text{O}^2 \\ \text{H}^2 \\ \text{N}^2 \end{array} \right\} 0.9454 \times 0.311 = 0.2940$$

$$\text{Sum} = 0.3176$$

$$\text{Heat carried out} = 0.3176 \times 282 = 89.56 \text{ Calories.}$$

$$\text{Per kilogram of coal} = 89.56 \times 3.43 = 307 \text{ Calories.}$$

$$\text{Proportion of calorific power} = \frac{307}{6669} = 4.6 \text{ per cent.}$$

The above result is, however, subject to a small correction, because some of the moisture in the coal goes undecomposed into the gases, and is not represented in the analysis of the dried gas. The amount of this moisture can be obtained with sufficient accuracy by finding how much moisture would be obtained by burning the dried gas from 1 kilogram of coal, and comparing this with the moisture which would be obtained from 1 kilogram of coal itself; the difference must represent the moisture accompanying the gas as water vapor, and which has not been included in the above computation.

Burning 1 cubic meter of gas, the H²O vapor is:

From CH ⁴ 0.0025 × 2	= 0.0050 cubic meters.
From H ² 0.1064 × 1	= 0.1064 " "
	0.1114 " "
Per kilo. of coal = 0.1114 × 3.43	= 0.3821 " "

But the weight of water vapor from burning 1 kilogram of coal has already been found to be (2) 0.4622 kilograms, the volume of which is

$$0.4622 \div 0.81 = 0.5706 \text{ cubic meters.}$$

Leaving, therefore, $0.5706 - 0.3821 = 0.1885$ cubic meters of water vapor as such accompanying the 3.43 cubic meters of (dried) gas from 1 kilogram of coal. This would take out

$$0.1885 \times 0.382 \times 282 = 20.3 \text{ Calories.}$$

Thus increasing the sensible heat in the gases to

$$307 + 20.3 = 327.3 \text{ Calories} = 4.9 \text{ per cent.} \quad (6)$$

[In reality, a still further correction should be made; viz.: to add in the moisture in the air used, because it would also reappear as moisture on final combustion of the gases. Its amount is found from the amount of air used, which, if 76 per cent. saturated at 9° would carry moisture having 0.76×7 mm. (if saturated) = 5.3 millimeters tension, which represents, barometer being 712 mm., 0.7 per cent. of the volume of the air used, or practically 0.9 per cent. of the volume of nitrogen in the air. Since the nitrogen in the gas represents almost entirely the nitrogen in the air used, the moisture to be accounted for from the air amounts to $0.5928 \times 0.009 = 0.0053$

cubic meters per cubic meter of gas, or = 0.0182 cubic meters per kilogram of coal burnt. This correction is altogether too small to affect the results in this case, but should be taken into account whenever the air used is warm and moist.]

(7) The calorific loss in conversion was 3122 Calories. Of this we have accounted for:

Lost by unburnt carbon in ashes.....	1237.7	Calories.
Sensible heat of gases (including moisture)....	327.3	“
Total.....	<u>1565.0</u>	“
Loss by radiation and conduction.....	= 1557.0	“(a)

Per 8 hours 5 minutes there is burnt 3214 kilograms of fuel, making the loss of heat by radiation and conduction per minute =

$$\frac{1557 \times 3214}{530} = 9,442 \text{ Calories.} \quad (b)$$

(8) At the conditions given, each cubic meter of moist air used contained 0.7 per cent. of its volume of moisture, making its percentage composition by volume:

	Water vapor.....	0.70	per cent.
Air {	Oxygen.....	20.65	“
	Nitrogen.....	79.65	“

The volume of gas produced per kilogram of coal is 3.43 cubic meters, of which 59.28 per cent. is nitrogen, equal to 2.0333 cubic meters, and weighing $2.0333 \times 1.26 = 2.562$ kilograms. Of this 0.0050 kilograms came from the coal itself, leaving 2.512 kilograms to come from the air, or $2.512 \div 1.26 = 1.9921$ cubic meters. This would correspond to $1.9921 \div 0.7965 = 2.5011$ cubic meters of moist air if measured at standard conditions. At 9° and 712 mm. pressure the real volume of moist air used at prevailing conditions, per kilogram of coal burnt, is

$$2.5011 \times \frac{273+9}{273} \times \frac{760}{712} = 2.76 \text{ cubic meters.} \quad (8)$$

It must not be thought that the conditions of working in the above producer represent good practice; they are very poor practice as far as concerns the utilization of the fuel. Many producers make gas having 75 to 90 per cent. of the

calorific power of the coal from which it is made, so that the losses by unburnt carbon and radiation and conduction in this case must be regarded as highly abnormal and very poor practice. The writer chose this example for calculating, because of the carefulness with which Jüptner and Toldt had collected the necessary data, and because it illustrated so well the principles to be employed in similar calculations.

Problem 17.

A gas producer run in Sweden uses saw-dust of the following composition:

Water.....	27.0 per cent.
Ash.....	0.5 "
Carbon.....	37.0 "
Hydrogen.....	4.4 "
Oxygen.....	30.6 "
Nitrogen.....	0.5 "

Assume that it is run by dry air and that 0.5 per cent. of ashes are made. The gas formed, dried before analysis, contains, by volume:

Carbon dioxide, CO_2	6.0 per cent.
Carbon monoxide, CO	29.8 "
Ethylene, C_2H_4	0.3 "
Methane, CH_4	6.9 "
Hydrogen, H_2	6.5 "
Nitrogen, N_2	50.5 "

The gas actually produced is partly dried before use by having its temperature reduced by cold water, in a surface condenser, to 29°C ., in order to increase its calorific intensity of combustion.

Required:

(1) The proportion of the moisture in the moist gas which is condensed out.

(2) The calorific intensity of the moist gas, if burned preheated to 800°C . by the theoretical quantity of air preheated also to 800°C .

(3) The calorific intensity of the dried gas, burnt under exactly similar conditions.

Solution:

(1) It is first necessary to find the weight or volume of water vapor accompanying the gas before condensation, next that accompanying it after passing the condenser. The first can be calculated best on the basis of the hydrogen present in the fuel and in the (dried) gas made from it; the difference is the hydrogen of the moisture removed before analysis, *i.e.*, the hydrogen of the moisture in the wet gas.

The first step is to find the volume of gas (dry) produced per unit of fuel, as follows:

$$\begin{aligned} \text{Carbon in 1 kilo. of fuel} &= 0.370 \text{ kilos.} \\ \text{Carbon in 1 m}^3 \text{ of gas} = \text{CO}^2 + \text{CO} + \text{CH}^4 + \\ &2\text{C}^2\text{H}^4 \text{ (0.060 + 0.298 + 0.069 + 0.006) } \times 0.54 = 0.2338 \text{ "} \\ \text{Dry gas per kilo. of fuel} = \frac{0.370}{0.2338} &= 1.5825 \text{ m}^3 \end{aligned}$$

The next step is to calculate the water which would be formed by the combustion of 1 kilogram of fuel:

$$\begin{aligned} \text{Water present in fuel} &\dots\dots\dots 0.270 \text{ kilos.} \\ \text{Water produced by hydrogen} &\dots\dots\dots 0.396 \text{ "} \\ \text{Total} &= 0.666 \text{ "} \end{aligned}$$

$$\text{Volume at standard conditions} = \frac{0.666}{0.810} = 0.8222 \text{ m}^6$$

From this we subtract the moisture which would be produced by the combustion of the 1.5825 cubic meters of dry gas, obtained as follows:

$$\begin{aligned} \text{Water from ethylene} &= 0.003 \times 2 \times 1.5825 \text{ m}^3 \\ \text{Water from methane} &= 0.069 \times 2 \times 1.5825 \\ \text{Water from hydrogen} &= \frac{0.065 \times 1 \times 1.5825}{= 0.209} \times 1.5825 = 0.3307 \text{ m}^3 \end{aligned}$$

$$\begin{aligned} \text{Difference} &= \text{water vapor to 1.5825 m}^3 \text{ of dried gas} \\ &= 0.8222 - 0.3307 = 0.4915 \text{ m}^3 \\ &= 0.4915 \div 1.5825 = 0.3106 \text{ m}^3 \text{ per 1 m}^3 \end{aligned}$$

of dried gas, as analyzed

This is to be compared with the amount of moisture accompanying the same quantity of (dried) gas as it escapes from the condenser. This is obtained directly from the fact that the gas escaping will be saturated with moisture at 29° C., that the latter will, therefore, have a tension of 30 millimeters (tables), and that, assuming the barometer normal (760 mm.), the partial tensions of moisture and gas proper are as 30 to 760—30, or as 30 to 730. Since their respective volumes (if both were measured separately at normal pressures) are in the same proportion, it follows that each cubic meter of (dry) gas is accompanied by $30 \div 730 = 0.0411$ cubic meters of uncondensed moisture.

The respective quantities of moisture accompanying 1 cubic meter of dry, uncondensable gas, are, therefore, 0.3106 before cooling and 0.0411 after cooling, showing that 13.5 per cent. of all the moisture escapes condensation, and that, therefore,

$$86.5 \text{ per cent. of moisture is condensed.} \quad (1)$$

(2) The wet gas has a calorific power, calculating on the basis of 1 cubic meter of dried gas analyzed:

$$\begin{array}{rcl} \text{CO} & 0.298 \times 3,062 & = 912.5 \text{ Calories.} \\ \text{C}^2\text{H}^4 & 0.003 \times 14,480 & = 43.4 \quad \text{"} \\ \text{CH}^4 & 0.069 \times 8,598 & = 593.3 \quad \text{"} \\ \text{H}^2 & 0.065 \times 2,613 & = 169.8 \quad \text{"} \\ & \text{Total} & = \underline{1719.0} \quad \text{"} \end{array}$$

There is added to this available heat, when burned, the sensible heat in the gas itself, at 800° C., and also that of the necessary air, also at 800°.

Heat in gas:

$$\begin{array}{rcl} \text{CO, H}^2, \text{N}^2 & = 0.630 \text{ m}^3 \times 0.3246 & = 0.2045 \text{ Cals. per 1}^\circ \\ \text{CO}^2 & = 0.060 \text{ m}^3 \times 0.5460 & = 0.0328 \quad \text{"} \\ \text{CH}^4 & = 0.069 \text{ m}^3 \times 0.4485 & = 0.0309 \quad \text{"} \\ \text{C}^2\text{H}^4 & = 0.003 \text{ m}^3 \times 0.50 & = 0.0015 \quad \text{"} \\ \text{H}^2\text{O} & = 0.3106 \text{ m}^3 \times 0.460 & = 0.1429 \quad \text{"} \\ & \text{Calorific Capacity} & = \underline{0.4126} \quad \text{"} \end{array}$$

$$\text{Total sensible heat} = 0.4126 \times 800 = 330.1 \text{ Calories.}$$

The air required theoretically is:

For CO	0.298 m ³	= 0.1490 m ³ oxygen
For C ² H ⁴	0.003 m ³	= 0.0090 m ³ "
For CH ⁴	0.069 m ³	= 0.1380 m ³ "
For H ²	0.065 m ³	= 0.0325 m ³ "
	Sum	= 0.3285 m ³ "
		= 1.58 m ³ air

Heat in this at 800° = 1.58 × 0.3246 × 800 = 410.3 Calories.

Sum total of heat going into the products:

Developed by combustion.....	1719.0	Cals.
Sensible heat in gas.....	320.4	"
Sensible heat in air.....	410.3	"
Total.....	<u>2459.4</u>	"

The products of the combustion are CO², H²O and N², as follows: CO² = 0.060 (in gas) + 0.298 (from CO) + 0.006 (from C²H⁴) + 0.069 (from CH⁴) = 0.433 m³.

H²O = 0.311 (with gas) + 0.006 (from C²H⁴) + 0.138 (from CH⁴) + 0.065 (from H²) = 0.520 m³.

N² = 0.505 (in gas) + [1.58 - 0.33 = 1.25] (from air) = 1.755 m³.

Since the 2459.4 Calories remains as sensible heat in the above products, at some temperature t , we have

Heat capacity of the CO ²	= 0.433 (0.37 + 0.00022t)
Heat capacity of the H ² O	= 0.520 (0.34 + 0.00015t)
Heat capacity of the N ²	= 1.755 (0.303 + 0.000027t)
Heat capacity of the products	= <u>0.8688 + 0.00022065t</u>

and the calorific intensity t must be

$$t = \frac{2459.4}{0.8688 + 0.00022065t}$$

whence

$$t = 1907^\circ \quad (2)$$

(3) When the dried gas is burned under similar conditions, the only difference is that 0.2695 m³ of water vapor are absent from the gas and from the products, having been condensed.

This reduces the available heat by the sensible heat in this much water vapor at 800°, viz.:

$$0.2695 \times 0.460 \times 800 = 99.2 \text{ Calories,}$$

and decreases the calorific capacity of the products by

$$0.2695 (0.34 + 0.00015t).$$

Our equation, therefore, becomes

$$t = \frac{2360.2}{0.7772 + 0.00018023t}$$

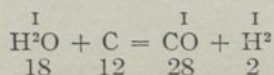
whence

$$t = 2056^\circ$$

The increased efficiency of the dried gas for obtaining high temperatures is too evident to need further comment, the difference being in round numbers 150° C., equal to 270° F., in favor of the dried gas.

2. MIXED GAS PRODUCERS.

This class of producers are those most commonly used. In them a moderate amount of steam or vapor of water passes with the air into the fire, and is decomposed, producing carbon monoxide and hydrogen gases by the reaction:

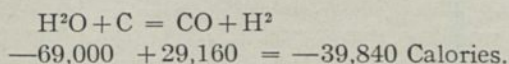


which may be read as follows: One volume of steam forms one volume of carbon monoxide and one volume of hydrogen; or eighteen parts by weight of water vapor act upon twelve parts of solid carbon, producing twenty-eight parts of carbon monoxide and two parts of hydrogen. If we speak of kilograms as the above weights, then we can call each "volume" spoken of 22.22 cubic meters; or if we call the weights ounces avoirdupois, each "volume" represents 22.22 cubic feet.

The water vapor is admitted either automatically, as in the old Siemen's type of producer, where water was run into the ash pit to be evaporated by the heat radiated from the grate or by hot ashes falling into it, or as in the modern water-seal

bottom producer, where the ashes rest upon water in a large pan, and so are continually kept soaked by capillary action; or, finally, steam is positively blown under the grate, either as a simple steam jet, or, more economically, by using it in a steam blower, so as to have it produce by injector action an air blast sufficient to run the producer. In the latter case the proportions of air and steam may be regulated with precision, and the blast action produced makes the production and delivery of the gas practically independent of chimney draft. The use of steam also rots or disintegrates the ashes, preventing or breaking up masses of clinker, and so facilitating the removal of the ashes.

Steam or water vapor cools down the fire in the producer so that it runs cooler; at the same time gas is produced which is rich in hydrogen, and, therefore, of higher calorific power. This saves unnecessary waste of heat in the producer, and increases the efficiency of the gas in the furnace in which it is burnt. The scientific reasons for these facts are to be found in a consideration of the thermochemistry of the reaction by which steam is decomposed.



This would be the deficit in decomposing 18 kilograms of water if it starts in the liquid state. If, however, it is used as steam at 100° C., each kilogram contains 637 Calories of sensible heat, making $18 \times 637 = 11,466$ Calories altogether, leaving the deficit 28,374 Calories, or the deficit

$$\begin{aligned} &= 1,576 \text{ Calories per kilogram of steam decomposed.} \\ &= 2,364 \text{ Calories per kilogram of carbon thus burnt.} \end{aligned}$$

In making this calculation it might be objected that the steam used is often at three or four atmospheres pressure, and its temperature, therefore, over 100° C.; but it must not be overlooked that this steam expands suddenly to atmospheric tension, and that in so doing it cools itself to an amount roughly proportional to its excess pressure so that the expanded steam at atmospheric pressure is usually close to 100° C. When mixed with air, the temperature of the mixture is usually below 100°, some 40° to 50° C., and in this condition some of

the steam is possibly condensed to fog, but it must not be forgotten that the heat of condensation thus given out has been absorbed in raising the temperature of the admixed air, and therefore goes as sensible heat into the bed of burning fuel. For the purpose of calculation, we will, therefore, be very nearly right in assuming that we are dealing in each case with steam at 100° C., requiring the above calculated deficits to be made up, in order for the decomposition to proceed.

It will be evident that any heat thus used in the producer must be sensible heat of the hot carbon, which, if not so used, would be lost as sensible heat in the gases produced or radiated and conducted away from the producer. The basic process of the running of the producer is the burning of carbon to carbon monoxide, liberating 2,430 Calories per kilogram of carbon, which is $2,430 \div 8,100 = 30$ per cent. exactly of the calorific power of the carbon. This heat, if no water vapor gets into the producer, is lost as sensible heat of the hot gases and by radiation and conduction, and is thus largely a dead loss. In Problem 16, for instance, these items figured out 28.25 per cent. of the calorific power of the coal used. Now, the facts are, that while small producers need that much heat to keep them up to working temperature, large producers need very much less, and run far too hot if no steam is admitted to check the rise of temperature. In the largest producers the sensible heat in the gases, plus the losses by radiation and conduction, does not exceed 10 per cent. of the calorific power of the fuel. Out of the 30 per cent. of the calorific power of the carbon inevitably generated, only some 10 per cent. is, therefore, needed to supply the losses in a large producer, leaving 20 per cent. applicable to decomposing steam. We therefore have:

Per 1 Kilo. of Carbon Gasified.

Heat generated.....	2,430	Calories.
Necessary loss in a large producer.....	810	“
Useful for decomposing steam.....	1,620	“
Required to decompose 1 kilo, steam at 212° F. (69,000—11,466) ÷ 18 =	3,196	“
Maximum steam decomposable	$1,620 \div 3,196 = 0.507$	kilo.

Calculation, therefore, shows that about one-half of a unit weight of steam is the maximum which can be used per unit

weight of carbon burnt to carbon monoxide, consistent with keeping the producer at proper working temperature. This would be equal to

- 0.088 kilos. of steam per kilo. of air used.
- 0.088 pounds of steam per pound of air used.
- 0.114 kilos. of steam per cubic meter of air used.
- 0.007 pounds of steam per cubic foot of air used.

The above discussion is on the assumption that the bed of fuel in the producer is thick enough, and its temperature always high enough, to burn all the carbon to carbon monoxide. Such is only an ideal condition, for the irregular charging, descent and working of the fuel always allow of some carbon dioxide being produced, and the best regular gas usually contains 1 to 5 per cent. of dioxide, representing some 3 to 20 per cent. of the total carbon oxidized in the producer.

Assuming that on an average 10 per cent. of the carbon oxidized inevitably forms carbon dioxide, we can calculate under these more usual conditions how much steam can be used, because for each kilogram of carbon oxidized, 0.1 kilo. then gives us 8,100 Calories per kilogram instead of 2,430 in the producer, a surplus of

$$0.1 \times (8,100 - 2,430) = 567 \text{ Calories.}$$

over the conditions when only monoxide is formed. Instead of the 1,620 Calories available for decomposing steam we will now have 2,187 Calories, which will decompose

$$\frac{2,187}{3,196} = 0.684 \text{ kilo. of steam.}$$

which reckoned on the air used would be

- 0.108 kilos. of steam per kilo. of air used.
- 0.108 pounds of steam per pound of air used.
- 0.140 kilos. of steam per cubic meter of air used.
- 0.009 pounds of steam per cubic foot of air used.

The above proportions are those which cannot practically be exceeded, if producing gas as low as is usually possible in carbon dioxide.

[Working the producer comparatively cold, with excess of

steam, much larger proportions of carbon dioxide are formed and correspondingly larger proportions of steam are decomposed, but this manner of working is abnormal, is not unusual, and will be discussed under the next heading, treating of Mond gas.]

Making gas containing any given proportion of CO^2 to CO, by volume, the ratio thus obtained is identical with the proportionate weight of carbon oxidized to CO^2 and CO in the producer, and by the application of the principles just described it can be calculated how much steam can be used per unit of carbon oxidized, making proper allowance for losses by radiation, etc.

Illustration: A Siemen's producer with chimney draft produced gas containing, by volume, 4.3 per cent. CO^2 and 25.6 per cent. CO. How much steam could be used per pound of air used, assuming 50 per cent. of the heat generated by the oxidation of the carbon to be needed to run the producer?

Solution:

$$\text{Per cent. of carbon burnt to } \text{CO}^2 = \frac{4.3}{4.3+25.6} = 14.4 \text{ per cent.}$$

Heat generated by C to CO^2	$= 0.144 \times 8,100$	$= 1,166$ lb. Cal.
Heat generated by C to CO	$= 0.856 \times 2,430$	$= 2,080$ "
Heat generated per kilo. of C		$= 3,246$ "
Heat lost by radiation, etc. (50 per cent.)		$= 1,623$ "
Heat available for decomposing steam		$= 1,623$ "

$$\text{Steam decomposable} = \frac{1,623}{3,196} = 0.508 \text{ pounds.}$$

The above is expressed per kilogram of carbon oxidized, but the same proportion is true per pound. The air required per pound of carbon oxidized is found from the oxygen required to form CO and CO^2 :

Oxygen for C to CO^2	$= 0.144 \times 8.3$	$= 0.384$ lbs.
Oxygen for C to CO	$= 0.856 \times 4.3$	$= 1.141$ "
Total	$= 1.525$	"
Air	$= 6.608$	"
Volume of air	$= \frac{6.608}{0.0808}$	$= 81.8$ cu. feet.

$$\text{Steam per cubic foot of air} = \frac{0.508}{81.8} = 0.006 \text{ lbs.}$$

$$\text{Steam per pound of air} = \frac{0.508}{6.608} = 0.077 \text{ "}$$

$$\text{Air required per pound of steam} = 13.0 \text{ "}$$

It should easily be seen that whatever heat is absorbed in the producer in decomposing steam, is entirely recovered when the hydrogen thus produced is burnt and steam is reproduced. If then, in any case, it is possible to absorb in the producer, in the decomposition of steam, an amount of heat equal to say, 20 per cent. of the total calorific power of the fuel, then that 20 per cent. is regained and capable of being utilized when the hydrogen so produced is burnt in the furnace. In other words, 20 per cent. *less* of the calorific power of the fuel will be lost in the process of conversion into gas in the producer, and 20 per cent. *more* will be obtained in the burning of the gas when it is used. The great advantages of using steam judiciously are thus clearly evident.

Problem 18.

R. W. Hunt & Co. report the following tests made of the running of a Morgan continuous gas producer. Coal used, "New Kentucky" Illinois coal, run of mine. Composition:

Fixed carbon.....	50.87	per cent.
Volatile matter.....	37.32	"
Moisture.....	5.08	"
Ash.....	6.73	"
	<u>100.00</u>	"

The ultimate composition was:

Total carbon.....	69.72	"
Hydrogen.....	5.60	"
Nitrogen.....	2.00	"
Total sulphur.....	0.94	"
Oxygen.....	11.00	"
Moisture.....	5.08	"
Inorganic residue (less sulphur).....	6.66	"

The ash, on combustion, contains 1.12 per cent. of its weight

of sulphur (as FeS); the ashes obtained from the producer contain 4.66 per cent. of unburnt carbon.

The gas produced, dried, contained by volume:

Carbon monoxide (CO).....	24.5 per cent.
Marsh gas (CH ⁴).....	3.6 “
Ethylene (C ² H ⁴).....	3.2 “
Carbon dioxide (CO ²).....	3.7 “
Hydrogen (H ²).....	17.8 “
Oxygen (O ²).....	0.4 “
Nitrogen (N ²) (by diffusion).....	46.8 “

[The moisture and sulphur compounds in the gas not having been determined, we can calculate the former, and, for the purposes of calculation, are justified in assuming the sulphur present in the gas as H²S, and in subtracting it from the hydrogen. We will also assume that the moisture in the coal goes unchanged into the gases as moisture, and that all the steam used is decomposed. The 0.94 per cent. of sulphur in the coal will furnish 0.86 per cent. to the gases, because $6.73 \times 0.0112 = 0.08$ per cent. will go into the ash as ferrous sulphide. The 0.86 pound of sulphur would produce 0.91 pounds of H²S, equal in volume to 9.56 cubic feet per 100 pounds of coal used, or (since we will see later that 53.83 cubic feet of gas are produced per pound of coal) there will be 0.2 per cent. of H²S in the gases, leaving 17.6 per cent. of hydrogen.]

On the basis of above data and assumptions:

Required: (1) The volume of gas produced per pound of fuel used in the producer.

(2) The weight of steam used per 100 cubic feet of air blown in, assuming the air dry.

(3) The proportion of the total heat generated in the producer which is utilized in decomposing steam.

(4) The percentage of increased economy thus obtained reckoned on the calorific power of the fuel.

(5) The efficiency lost by unburnt carbon in the ashes.

(6) The efficiency of the gas, burnt cold, compared with the coal from which it is made.

Solution: (1) Per pound of coal burnt, there remains in the ashes $0.0673 \times (0.0466 \div 0.9534) = 0.0033$ pounds of unburnt carbon, leaving $0.06972 - 0.0033 = 0.6939$ pounds gasified.

One cubic foot of gas, at 32° F., contains the following weight of carbon:

$$\begin{aligned}
 \text{C in CO} &= 0.245 \times 0.54 \text{ ounces} \\
 \text{C in CH}^4 &= 0.036 \times 0.54 \text{ " } \\
 \text{C in C}^2\text{H}^4 &= 0.032 \times 1.08 \text{ " } \\
 \text{C in CO}^2 &= 0.037 \times 0.54 \text{ " } \\
 \text{Total} &= \frac{0.382}{0.01289} \times 0.54 \text{ " } \\
 &= 0.20628 \text{ ounces av} \\
 &= 0.01289 \text{ pounds av.}
 \end{aligned}$$

Gas produced, measured dry, per pound of coal, at 32° F.:

$$\frac{0.6939}{0.01289} = 53.83 \text{ cubic feet}$$

(2) If the moisture of the coal is assumed to pass unchanged into the gas, as moisture, then all the hydrogen in the dry gas, in any form or combination, must have come either from hydrogen in the coal or in the air blast. The hydrogen in the coal is given as 5.60 per cent. The hydrogen in the gas is calculated as follows, per cubic foot:

$$\begin{aligned}
 \text{H}^2 \text{ in H}^2 &= 0.176 \times 0.09 \text{ ounces.} \\
 \text{H}^2 \text{ in H}^2\text{S} &= 0.002 \times 0.09 \text{ " } \\
 \text{H}^2 \text{ in CH}^4 &= 0.036 \times 0.18 \text{ " } \\
 \text{H}^2 \text{ in C}^2\text{H}^4 &= 0.032 \times 0.18 \text{ " } \\
 \text{Total} &= 0.314 \times 0.09 \text{ " } \\
 &= 0.02826 \text{ ounces av.} \\
 &= 0.00177 \text{ pounds av.}
 \end{aligned}$$

Hydrogen in gas from 1 pound of coal:

$$0.00177 \times 53.83 = 0.0953 \text{ pounds.}$$

Hydrogen from decomposition of steam:

$$0.0953 - 0.0560 = 0.0393 \text{ pounds.}$$

Weight of steam decomposed per pound of coal used:

$$0.0393 \times 9 = 0.3537 \text{ pounds.}$$

To express this weight relatively to the air blown in, we must calculate the air used per pound of coal, as follows:

Nitrogen in gas per cubic foot

$$0.468 \times (14 \times .09) = 0.5897 \text{ oz. av.} \\ = 0.036856 \text{ lbs. av.}$$

Per pound of coal = $0.036856 \times 53.83 = 1.9840$ "

Subtract N² in 1 pound of coal = 0.0200 "

Leaves N² from air = 1.9640 "

Weight of air = $1.9640 \times \frac{13}{10} = 2.5532$ "

Volume of air = $2.5532 \times 16 \div 1.293 = 31.61$ cu. ft.

Steam used per 100 cubic feet of air blown in:

$$= \frac{0.3537}{31.61} \times 100 = 1.119 \text{ pounds.} \quad (2)$$

(3) The heat utilized in decomposing steam has been found to be 3,196-pound Calories per pound of steam at 212° F. We therefore, have the heat so used per pound of fuel used:

$$0.3537 \times 3,196 = 1,130\text{-pound Calories.}$$

This quantity must now be compared with the total heat generated in the producer, and the latter quantity can be determined in two ways: (1) We may subtract from the total calorific power of the coal the calorific power of the gas produced and of the unburnt carbon in the ashes; the difference must be the *net* heat generated in the producer, *i.e.*, the total heat generated minus that absorbed in decomposing steam. The total heat generated is the net heat thus calculated plus the heat absorbed in decomposing steam. (2) We may calculate the heat of formation of the CO and CO² in the gas, and assume that as the total heat generated in the producer. This method is not so accurate as (1).

The total calorific power of the coal is given as practically 7,747-pound Calories per pound, water formed being condensed, which would be decreased by the latent heat of vaporization, if the latter is assumed uncondensed. The deduction is $606.5 \times [(0.056 \times 9) + 0.0508] = 337\text{-pound Calories}$, leaving 7,410-pound Calories as the practical metallurgical calorific power of the fuel.

Calorific power of the gas (dried) per cubic foot:

CO	$0.245 \times 3,062 = 750.2$	ounce Cal.
CH ⁴	$0.036 \times 8,598 = 309.5$	"
C ² H ⁴	$0.032 \times 14,480 = 463.4$	"
H ²	$0.176 \times 2,613 = 459.9$	"
H ² S	$0.002 \times 5,513 = 11.0$	"
	Total = $\overline{1994.0}$	"
	= 124.6	pound Cal.

Calorific power of gas per pound of coal:

$$124.6 \times 53.83 = 6,707 \text{ pound Cal.}$$

Calorific power of carbon in ashes:

	$0.0033 \times 8,100 = 27$	"
	Sum = $\overline{6,734}$	"
Calorific power of 1 pound coal	= $\overline{7,410}$	"
Net heat lost in conversion	= $\overline{676}$	"
Used in decomposing steam	= $\overline{1,130}$	"
Gross heat generated in producer	= $\overline{1,806}$	"

Proportion of this utilized in decomposing steam:

$$\frac{1,130}{1,806} = 0.626 = 62.6 \text{ per cent.} \quad (3)$$

(4) We can state this result in another way, by saying that $1,806 \div 7,410 = 24.40$ per cent. of the calorific power of the fuel is generated in the producer, of which $1,130 \div 7,410 = 15.25$ per cent. is utilized to decompose steam, and 9.15 per cent. is lost by radiation, conduction and sensible heat in the gases. The calorific power of the gases represents $6,707 \div 7,410 = 90.50$ per cent. of the calorific power of the coal of which 9.15 per cent., however, is clear gain from the employment of steam. Reckoning on the total calorific power of the coal, the increased economy from the use of steam is 9.15 per cent. (4)

(5) The loss of calorific power by the unburnt carbon in the ashes is 27-pound Calories, or, on the whole heat available,

$$= \frac{27}{7,410} = 0.36 \text{ per cent.}$$

This loss is exceptionally low, and may be very profitably compared with the analogous loss of 18.6 per cent. occurring in the case discussed in Problem 16.

(6) This has already been calculated as

$$\frac{6,707}{7,410} = 90.50 \text{ per cent.}$$

on the assumption that the gases are burnt cold. If they are burnt hot, say issuing from the producer at 1200° F. (649° C.), and are burnt when at 1,000° F. (548° C.) their sensible heat at 1,000° F. will be added to their efficient heating power, and can be calculated with exactness, using the principle explained and used in requirement (6) of Problem 14. Under such conditions the total efficiency of the producer, reckoned on the calorific power of the coal used, approximates 95 per cent.

To be fair to everybody concerned, however, we must deduct from this the coal required to be burnt to raise the steam used. There is a little over one-third pound of steam used per pound of coal used in the producer. This requires in

ordinary boiler practice $\frac{1}{3} \times \frac{1}{8} = \frac{1}{24}$ pound of coal, or about 4

per cent. of the weight of fuel burnt in the producer. The results of the previous calculation must, therefore, be diminished in this proportion, if the steam has to be raised by burning coal under boilers. Under these conditions (6) becomes:

$$90.50 \div 1.04 = 87 \text{ per cent. efficiency.} \quad (6)$$

If the steam can be obtained from waste gases of a blast furnace, or from the hot producer gases themselves (in case they are going to be burnt cold), then no such deductions need be made. It is very evident, however, that if 9.15 per cent. greater efficiency is gained by burning 4 per cent. more coal to raise the steam, that the net gain would be only 5.15 per cent. Even under these conditions it pays to use steam, because of the greater calorific intensity of the richer gas, the usefulness of the steam for supplying air blast, and the rotting of the clinkers therewith obtained.

3. MOND GAS.

In the Mond producer, an excess of steam is introduced with the heated air used for combustion; the producer is thus run much colder than the ordinary producer, and far more carbon dioxide is present in the gas. In fact, the gas, compared with ordinary producer gas, is very high in carbon dioxide (10 to 20 per cent.), very high in hydrogen (20 to 30 per cent.), very low in carbon monoxide (10 to 15 per cent.), low in nitrogen (40 to 50 per cent.), and carries an extraordinary amount of undecomposed moisture. The fuel used is low-grade bituminous slack, and the object of using so much steam is to keep the temperature in the producer so low that a maximum amount of the nitrogen in the coal is evolved as ammonia. The gas is cooled to ordinary temperature by contact with water spray, so that all but a small amount of moisture is condensed, the ammonia is removed by dilute sulphuric acid, and the cold nearly dry gas is then used for gas engines or in furnaces.

The calorific power of the gas is not low, because the high proportion of hydrogen compensates for the low carbon monoxide, while the great heat evolved by the large formation of carbon dioxide has been mostly absorbed in decomposing steam, and is, therefore, potentially present in the gas in the form of hydrogen.

Problem 19.

Bituminous slack coal used in Mond producers for generating gas for a gas-engine power plant contained:

Moisture.....	8.60 per cent.
Carbon.....	62.69 "
Hydrogen.....	4.57 "
Oxygen.....	10.89 "
Nitrogen.....	1.40 "
Ash.....	10.42 "

Calorific power, determined in a bomb calorimeter, water condensed, 6,786 Calories per unit of dried fuel. Ashes produced 268 pounds per ton (2,240 pounds) of moist slack used; contains 12 per cent. of carbon.

Air used for running is heated to 300° C. by the waste heat of producer gases, and carries in 2½ tons of water as steam (at

same temperature) for every ton of fuel burnt. The steam is generated by a tubular boiler run by the escape gases from the gas engines, but is heated from 100° C. to 300° C. by the waste heat of the producer gases. The latter escape from the producer at 350° C.

Composition of waste gases passing out of condensers at 15° C.:

Carbon monoxide (CO).....	11.0	per cent
Hydrogen (H ²).....	27.5	“
Marsh gas (CH ⁴).....	2.0	“
Carbonic oxide (CO ²).....	16.5	“
Nitrogen (N ²).....	41.3	“
Water vapor (H ² O).....	1.7	“
	<hr/>	
	100.0	“

Assume all the nitrogen of the fuel to form ammonia gas NH³.

Required:

- (1) The calorific power of the Mond gas.
- (2) The volume of gas produced per ton of fuel used.
- (3) The efficiency of the producer.
- (4) The weight of steam which is decomposed in the producer.
- (5) The proportion of the calorific power of the fuel saved to the gas by the decomposition of steam.
- (6) The proportion of the heat generated in the producer which is saved to the gas by the decomposition of steam.
- (7) The proportion of the calorific power of the coal lost from the producer by radiation and conduction.

Solution: (1) One cubic foot of the gas at 0° C. would generate the following amounts of heat (water uncondensed).

$$\begin{aligned}
 \text{CO} &= 0.110 \text{ cubic feet} \times 3062 = 336.8 \text{ ounce Calories.} \\
 \text{H}^2 &= 0.275 \text{ cubic feet} \times 2613 = 718.6 \quad \text{“} \quad \text{“} \\
 \text{CH}^4 &= 0.020 \text{ cubic feet} \times 8598 = 172.0 \quad \text{“} \quad \text{“} \\
 \text{Total} &= 1227.4 \quad \text{“} \quad \text{“} \\
 &= 76.7 \text{ pound} \quad \text{“} \\
 &= 138.1 \text{ B. T. U.} \\
 \text{Per cubic meter} &= 1227.4 \text{ kilo.} \quad \text{“}
 \end{aligned}$$

If measured at 15° C. (60° F.) the above values will be reduced by the factor $273 \div (273 + 15)$, and become

$$\begin{aligned} \text{Per cubic foot} &= 72.7 \text{ pound Calories.} \\ \text{Per cubic meter} &= 1163 \text{ kilo.} \quad \text{“} \quad (1) \end{aligned}$$

(2) Carbon in 1 cubic foot of gas at 0° C.:

$$\begin{aligned} \text{In CO} & 0.110 \times 0.54 \text{ ounces} \\ \text{In CH}_4 & 0.020 \times 0.54 \quad \text{“} \\ \text{In CO}_2 & 0.165 \times 0.54 \quad \text{“} \\ & \underline{0.295} \times 0.54 \quad \text{“} = 0.1593 \text{ ounces} \\ & = 0.009956 \text{ pounds} \end{aligned}$$

Carbon going into gas per pound of fuel burnt:

$$\text{Carbon in fuel} \quad \quad \quad 0.6269 \text{ pounds}$$

$$\text{Carbon in ashes} \quad \frac{268}{2240} \times 0.12 = 0.0144 \quad \text{“}$$

$$\text{Carbon in gas} \quad \quad \quad = 0.6125 \quad \text{“}$$

Volume of gas (at 0° C.) per pound of fuel used:

$$\frac{0.6125}{0.009956} = 61.52 \text{ cubic feet}$$

$$\begin{aligned} \text{Per ton of 2240 pounds} & \quad \quad \quad = 137,805 \text{ cubic feet} \\ \text{At 15° C. (60° F.)} & \quad \quad \quad \end{aligned}$$

$$= 137,805 \times \frac{273 + 15}{273} = 145,375 \quad \text{“} \quad \text{“} \quad (2)$$

(3) The calorific power of the dried fuel is given as 6,786 Calories per pound, water condensed. Since one pound of wet fuel contains $100 - 8.60 = 91.40$ per cent. dried fuel, the calorific power of 1 pound of wet fuel, moisture condensed, is

$$6,786 \times 0.9140 = 6,202 \text{ pound Calories.}$$

But, 1 pound of wet fuel would produce, on combustion,

$$0.0860 + 9 (0.0457) = 0.4973 \text{ pounds moisture,}$$

which, remaining vaporized at 15°, would retain

$$0.4973 \times 596 = 296 \text{ Calories,}$$

leaving the net metallurgical calorific power as

$$6,202 - 296 = 5,906 \text{ Calories.}$$

The 61.52 cubic feet of gas produced per pound of moist fuel will have a calorific power, burnt cold, of

$$61.52 \times 76.7 = 4,719 \text{ Calories.}$$

making the efficiency of the producer, on fuel consumed in it,

$$\frac{4,719}{5,906} = 0.799 = 79.9 \text{ per cent.} \quad (3)$$

The above figure is true only on the assumption that the steam used is obtained from waste heat, and therefore does not require the combustion of extra fuel

(4) The gas produced contains, per cubic foot, the following amount of hydrogen, free and as CH^4 :

As H^2 0.275 cubic feet $\times 0.09$		= 0.02475 ounces.
As CH^4 0.040 cubic feet $\times 0.09$		= 0.00360 "
	Sum	= <u>0.02835</u> "
		= 0.001772 pounds.
Per pound moist fuel = 0.001772×61.52		= 0.1090 "
Present as ammonia gas $0.0140 \times (3 \div 14)$		= <u>0.0010</u> "
Total (not including H as water)		= <u>0.1100</u> "
Hydrogen in 1 pound of coal		= 0.0457 "
Hydrogen from decomposition of steam		= <u>0.0642</u> "
Water decomposed in the producer		= 0.5787 "(4).

Since the steam introduced weighs 2.5 pounds for every pound of fuel burnt, we see that only

$$\frac{0.5787}{2.5} = 0.2315 = 23.15 \text{ per cent.}$$

of the steam introduced is decomposed.

[In the writer's opinion this unused 76.85 per cent. can only pass in and pass out carrying out sensible heat, and it seems a very wasteful method of keeping down the temperature in the producer. From the standpoint of regarding the 2 pounds of steam as a mere absorber of sensible heat, it could probably be replaced by some of the gases of combustion from the gas engine or open-hearth furnace. The products of combustion of the above gas would contain approximately

Nitrogen.....	68.7 per cent.
Carbon dioxide.....	14.7 "
Water vapor.....	16.6 "

And if the $\frac{1}{2}$ pound of water vapor decomposed in the producer were thus supplied, it would bring in, per pound of coal burnt,

Nitrogen.....	41.2 cubic feet.
Carbon dioxide.....	8.8 “
Water vapor.....	9.9 “

And if the CO^2 thus introduced were reduced to CO , as it probably would be, the gases would receive from this source

Nitrogen.....	41.2 cubic feet.
Carbon monoxide.....	27.5 “
Hydrogen.....	9.9 “

Thus producing gas quite up to standard as regards combustibles, while the heat absorbed in the reduction of CO^2 to CO would cool the fire down quite as effectually as the extra steam now used.]

(5) The steam decomposed, 0.5787 pounds per pound of fuel burnt, may be assumed to be at 100° C. on entering the fire, and to therefore absorb 3,196-pound Calories per pound of steam decomposed. The heat absorbed in the producer, and thus transferred into potential calorific power is, therefore

$$3196 \times 0.5787 = 1850 \text{ pound Calories,}$$

which expressed in per cent. of the calorific power of the fuel is

$$\frac{1850}{5906} = 0.313 = 31.3 \text{ per cent} \quad (5)$$

(6) The heat generated in the producer equals the calorific power of the coal minus the heat lost by carbon in the ashes, minus the calorific power of the gases, plus the heat absorbed in decomposing steam. The loss by carbon in the ashes is

$$\frac{268}{2240} \times 0.12 \times 8100 = 117 \text{ Calories.}$$

The heat generated in the producer is, therefore,

$$5906 - 117 - 4719 + 1850 = 2920 \text{ Calories,}$$

equal to $2920 \div 5906 = 49.4$ per cent. of the calorific power of

the coal. Of this, 1850 Calories is absorbed in decomposing steam, which is $\frac{1850}{2920} = 63.4$ per cent. of the total heat generated. (6)

(7) There are 2922 Calories generated in the producer, of which 1850 are absorbed in decomposing steam, leaving 1072 Calories to supply radiation and conduction and as sensible heat in the hot gases, to which must be added the sensible heat in the hot air and steam used at 300° C.

The air used per pound of coal is found from the nitrogen in the gases:

Nitrogen in 1 cubic foot of producer gas	= 0.413 cubic foot
Nitrogen in 61.52 cubic foot of producer gas	= 25.40 "
Air used = $25.4 \div 0.792$	= 32.08 "
Steam used = $(2.5 \times 16) \div 0.81$	= 49.40 "

Heat in steam and air at 300° C. (from 15° C.):

$$\begin{aligned}
 32.08 \times 0.3116 \times 285 &= 2850 \text{ ounce Calories} \\
 49.40 \times 0.3872 \times 285 &= 5450 \text{ " " } \\
 \text{Sum} &= \underline{8300} \text{ " " } \\
 &= 519 \text{ pound Calories}
 \end{aligned}$$

Total heat radiated, conducted and in hot gases:

$$1070 + 519 = 1589 \text{ Calories.}$$

The heat in the hot gases is as follows, per cubic foot of gas produced:

$$\begin{aligned}
 \left. \begin{array}{l}
 \text{CO } 0.110 \times 0.313 \times 335 \\
 \text{H}^2 \text{ } 0.275 \times 0.313 \times 335 \\
 \text{N}^2 \text{ } 0.413 \times 0.313 \times 335
 \end{array} \right\} &= 83.7 \\
 \text{CO}^2 \text{ } 0.165 \times 0.450 \times 335 &= 24.9 \\
 \text{CH}^4 \text{ } 0.020 \times 0.460 \times 335 &= 3.1 \\
 \text{Sum} &= \underline{111.7} \text{ ounce Calories.} \\
 &= 7.0 \text{ pound Calories.}
 \end{aligned}$$

Per pound of coal burnt:

$$7.0 \times 61.52 = 430 \text{ pound Calories}$$

To this must be added the heat in undecomposed water vapor in the gases, as follows:

Steam used per pound of coal	=	2.50	pounds
Steam decomposed per pound of coal	=	0.58	"
Steam remaining in gases	=	1.92	"
Moisture in coal	=	0.086	"
Total in gases	=	2.006	"
Volume = $(2.006 \times 16) \div 0.81$	=	39.6	cubic feet

Heat contained in this at 350° C.:

$$39.6 \times 0.395 \times 335 = 5240 \text{ ounce Calories}$$

$$= 328 \text{ pound Calories}$$

Total heat in producer gases:

$$430 + 328 = 758 \text{ Calories}$$

Heat lost by radiation and conduction:

$$1589 - 758 = 831 \text{ Calories}$$

Proportion of calorific power of coal thus lost:

$$\frac{831}{5906} = 0.141 = 14.1 \text{ per cent.} \quad (7)$$

When Mond gas is heated in the regenerator of an open-hearth furnace it changes considerably in composition, as is shown by the following analyses made by Mr. J. H. Darby, on gas dried before analysis:

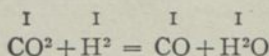
	<i>Before Regenerator.</i>	<i>After Regenerator.</i>
Carbonic acid gas, CO ²	17.8	10.5
Carbon monoxide, CO.....	10.5	21.6
Ethylene, C ² H ⁴	0.7	0.4
Methane, CH ⁴	2.6	2.0
Hydrogen, H ²	24.8	17.7
Nitrogen, N ²	43.6	47.8
	100.0	100.0

The above changes are very interesting, and their discussion profitable. Before heating, the gas burns with a non-luminous

flame; after heating, it burns with a brilliant white flame. Let us inquire:

- (1) What chemical change occurs during the heating?
- (2) What are the relative volumes of the gas before and after heating (excluding water)?
- (3) What change in the calorific power is produced by the heating?

(1) An inspection of the analyses shows undoubtedly that at a high temperature the CO^2 cannot hold all its oxygen in the presence of such a large amount of hydrogen, and that the following reaction must occur:



The figures given do not check exactly, but assuming that the above reaction takes place, we can find to what extent, by expressing the composition of the gas after heating for the same amount of *nitrogen* as was in the gas before heating, since this gas is unchanged:

	<i>Before Heating.</i>	<i>After Heating.</i>	<i>Loss or Gain.</i>
CO^2	17.8	9.6	-8.2
CO	10.5	19.7	+9.2
H^2	24.8	16.1	-8.7
N^2	43.6	43.6	0.0

Since, according to the reaction written, the volume of CO^2 reduced to CO will be equal to the volume of H^2 thus consumed, and will produce an equal volume of CO ; the above table proves, within the probable limits of error, that the reaction written actually takes place.

The separation of luminous carbon is probably due to the splitting up of C^2H^4 .

The relative volumes of the heated and unheated gases will be inversely as the percentage of nitrogen in each (since this gas is unchanged), viz.: as 47.8 to 43.6, or as 100 to 91.2. The contraction, 8.8 parts, would again correspond almost exactly to the amount of water formed in the assumed reaction, which would be equal to the hydrogen so used, thus giving another check on the validity of the reaction assumed to take place.

The calorific power of 1 cubic foot of original gas is:

CO	0.105 × 3,062 =	321.5	ounce	Calories
C ² H ⁴	0.007 × 14,480 =	101.4	"	"
CH ⁴	0.026 × 8,598 =	223.5	"	"
H ²	0.248 × 2,613 =	648.0	"	"
	Sum =	1294.4	"	"
		=	80.9	pound
Per 100 cubic feet	=	8090	"	"

The calorific power of 1 cubic foot of heated gas is:

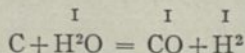
CO	0.216 × 3,062 =	661.4	ounce	Calories
C ² H ⁴	0.004 × 14,480 =	57.9	"	"
CH ⁴	0.020 × 8,598 =	172.0	"	"
H ²	0.177 × 2,613 =	462.5	"	"
	Sum =	1353.8	"	"
		=	84.6	pound

For 91.2 cubic feet the calorific power would be $84.6 \times 91.2 = 7715$ pound Calories.

The net conclusion is that the heated gas (aside from its sensible heat) gives less heat by combustion in the furnace per unit of coal gasified in the producers than the corresponding quantity of unheated gas; but the difference is only some 4 per cent. On the other hand, the calorific power of the heated gas per cubic foot is some 5 per cent. greater than that of the unheated gas, and, therefore, its calorific intensity will have been increased by the heating—quite aside from the question of its temperature being higher, and therefore its sensible heat greater.

4. WATER GAS.

This gas is made intermittently, by first burning part of the fuel until the fire is very hot, and then introducing steam, cool or superheated, into the fire. The reaction producing the gas is:



And if the reaction is complete, and only carbon is present as fuel, the gas produced is theoretically composed of equal parts by volume of CO and H², the volume of each of these being equal to that of the steam used (if measured at the same temperature and pressure).

Deviations from this ideal composition are caused in practice by the occurrence of undecomposed steam in the gas, also of CO^2 and N^2 , which come from the residual gas formed during the heating up of the fire, some of which will get into the first portion of the water-gas produced, and also hydrocarbons, tar and ammonia from the distillation of the fuel. A typical analysis of water-gas, given by Mr. W. E. Case, is:

Hydrogen (H^2).....	48.0
Carbon monoxide (CO).....	38.0
Methane (CH^4).....	2.0
Carbon dioxide (CO^2).....	6.0
Nitrogen (N^2).....	5.5
Oxygen (O^2).....	0.5

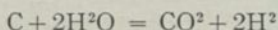
The production of water-gas is more expensive than that of other artificial producer gases, because of the large amount of steam necessarily required, the heat lost during the heating up, and the essentially intermittent character of the operation. Its essential advantages are its very high proportion of combustibles, averaging 90 per cent, and the consequent high calorific intensity which it is capable of producing. (Uncarburetted, it is well known that water-gas is a valuable domestic fuel, and illuminant when used in mantle burners; carburetted, it forms our principal illuminating gas, and as such is manufactured on an immense scale. We will treat here only of its metallurgical uses.)

Discussing the manufacture of the gas, the first step is the heating up of the fuel. This is accomplished by blowing air through it. At this point we can distinguish two systems. The older one is that of blowing in air under moderate pressure, which passes through the fire at moderate velocity, and produces a fair grade of ordinary producer gas. This gas is either wasted, or burned in furnaces requiring such quality of gas, or burned in regenerators where heat is stored up to be utilized in the next stage in superheating steam. The newer system is to blow in air at high pressure, such that a large percentage of carbon dioxide remains in the gases, thus nearly completely burning what carbon is oxidized, and storing up a corresponding quantity of heat in the remaining carbon. The incombustible gases produced are passed through a recuperator

or regenerator, where their sensible heat is partly communicated to the steam used, so as to superheat it when forming water-gas. This system consumes the minimum of carbon in "heating up" the fuel, saves time in this unproductive period, and allows the producer to be run longer "on steam." In practice the fuel is probably raised to an average temperature of 1500° C. during the heating up.

We can calculate the efficiency of this heating up, that is, the proportion of the calorific power of the carbon burnt which is stored up in the remaining fuel, if we know how much fuel is in the producer, how much air is blown through, the composition of the gases produced, and the average rise in temperature of the fuel. Since this operation is, however, only supplementary to the real formation of water-gas by the decomposition of steam, we will first make calculations upon the cooling down period, during which water-gas is made.

During the use of steam the reaction absorbs heat, and the producer rapidly cools. Steam is passed through until the temperature of the fuel is 800° C., and must then be stopped, because between 800° and 600° the reaction is mostly



resulting in a rapid increase of CO² in the gas. The heat to decompose steam is furnished partly by the oxidation of carbon to CO, and partly by the sensible heat in the carbon itself. Since the carbon, from temperatures of about 1000° C. up has a specific heat of 0.5, we can easily calculate how much steam can be decomposed before the temperature falls to 800°.

Problem 20.

A Dellwick-Fleischer water-gas producer contains 3 tons of coke (90 per cent. carbon), heated up to 1500° C. Steam, heated to 300° C., is passed through for 8 minutes, until the temperature of the gas escaping is 700° C., or 800° at the fuel bed. The composition of the gas is (Prof. V. B. Lewes):

Hydrogen.....	50.0
Carbon monoxide.....	40.0
Carbon dioxide.....	5.0
Oxygen.....	1.0
Nitrogen.....	4.0

Assume 9000 Calories per minute lost by radiation and conduction.

Required: (1) The amount of steam used in the 8 minutes
(2) The volume of gas produced in the 8 minutes.

(1) The amount of steam which could have been used is limited by the available heat to decompose it. The latter is furnished by

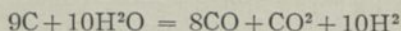
- (a) Oxidation of carbon to monoxide.
- (b) Oxidation of carbon to dioxide.
- (c) Sensible heat of the carbon and ash of fuel.
- (d) Sensible heat of the steam used.

While the items of heat absorption and loss are:

- (e) Decomposition of the steam.
- (f) Sensible heat in the gases.
- (g) Radiation and conduction.

The simplest way to arrive at a solution is to make a few necessary assumptions, and to then let X represent the weight of steam used. The assumptions are that the average temperature of the fuel bed falls to 1000° C., that the average temperature of the escaping gases is $(1500 + 700) \div 2 = 1100^\circ \text{C.}$, that the average specific heat of carbon in the range 1000—1500 is 0.5, and of the ash of the fuel 0.25. Then, casting up a heat balance sheet in terms of X, we can finally arrive at an expression for the heat which was available during the 8 minutes for decomposing steam, and thus at the weight of steam decomposed, and (making this equal to X) at a solution.

(a) The analysis of the gas shows that eight times as much carbon was burnt to monoxide as to dioxide, making the equation of combustion:



By weight, $8 \times 12 = 96$ parts of carbon was burnt to CO per $10 \times 18 = 180$ parts of steam used, or 0.533 parts per one part of steam. The heat generated in forming monoxide is, therefore:

$$0.533 \times X \times 2430 = 1296 \text{ X Calories.}$$

(b) Only one-eighth as much carbon burns to dioxide, giving, therefore, as the heat evolved:

$$(0.533 \div 8) \times X \times 8100 = 540 \text{ X Calories.}$$

(c) 3000 kilos. of fuel, representing 2700 kilos. of carbon and 300 kilos. of ash, cool from 1500° to 1000°:

$$\begin{aligned} 2700 \times 0.50 \times 500 &= 675,000 \text{ Calories} \\ 300 \times 0.25 \times 500 &= 37,500 \quad \text{"} \\ \text{Sum} &= 712,500 \quad \text{"} \end{aligned}$$

(d) $X \div 0.81$ will be the volume of the steam used at normal conditions, which brings in considered only as vapor, at 300°:

$$(X \div 0.80) \times 0.385 \times 300 = 93.5 X \text{ Calories.}$$

The sum total of (a) + (b) + (c) + (d) gives the total available heat, viz.:

$$1929.5 X + 712,500 \text{ Calories.}$$

(e) The steam used requires for its decomposition, considered theoretically as cold steam, producing cold products:

$$(X \div 9) \times 29,042 = 3227 X \text{ Calories}$$

(f) The gas being 50 per cent. hydrogen, and the latter being equal to the volume of steam used, the volume of gas must be $2 \times (X \div 0.81)$, which multiplied by the mean specific heat of gas of this composition between 0° and 1100° per cubic meter, and by the temperature, will give the heat thus carried out of the producer:

$$\begin{aligned} 2 (X \div 0.81) \times 0.347 \times 1100 &= 942.5 X \text{ Calories} \\ \text{(g)} \quad 9000 \times 8 &= 72,000 \text{ Calories.} \end{aligned}$$

The sum total of (e) + (f) + (g) gives the total heat distribution, viz.:

$$4,169.5 X + 72,000 \text{ Calories.}$$

Since the heat available equals the heat distributed:

$$\begin{aligned} 1,929.5 X + 712,500 &= 4,169.5 X + 72,000 \\ \text{or} \quad X &= 286 \text{ kilograms} \end{aligned} \quad (1)$$

(2) The volume of this steam, at assumed standard conditions, would be

$$286 \div 0.81 = 353 \text{ cubic meters,}$$

and of gas, since it is 50 per cent. hydrogen,

$$353 \times 2 = 706 \text{ cubic meters.}$$

The above figures represent the maximum attainable production, on the assumption that sufficient steam-generating power is available to furnish the steam, and that the fuel in the producer is of small size and the bed so uniform that the production of gas is regular all over it. In practice, figures considerably below this are attained, but it is always well to know the possible maximum which is attainable.

Problem 21.

In a Dellwick-Fleischer water-gas producer the heating up is accomplished in 2 minutes by blast from a Root blower, furnishing air through a 9.5 inch pipe at a total water-gauge pressure of 19 inches of water, temperature of air 15° C. The gases escaping from the producer analyze:

Carbon dioxide	17.9	per cent.
Carbon monoxide.....	1.8	"
Nitrogen.....	78.6	"
Oxygen.....	1.7	"

Temperature of waste gases 900° C.; heat lost by radiation and conduction 9000 Calories per minute; assume producer to contain 3000 kilos. of fuel, consisting of 90 per cent. carbon and 10 per cent. ash.

Required: (1) The average rise in temperature of the fuel bed.

(2) The proportion of the heat generated which is thus stored up as useful heat for producing water-gas.

(3) Assuming that the production of water-gas lasts 8 minutes, during which 2500 Calories are absorbed from the fuel bed per kilogram of steam used, what should be the steam supply in kilograms per minute?

(4) The ratio between the volume of air supplied during the blowing up period and the weight of steam used in the gas-making period.

Solution: (1) We must first find the amount of air furnished by the blower. To do this, we calculate the pressure head in terms of air at 15° C., instead of water, and then apply the well-known formula $V = \sqrt{2g \cdot h}$. Water is 772 times as heavy as air at 0° C., and, therefore, 19 inches of water pressure would represent $19 \times 772 \div 12 = 1222$ feet of air pressure (that is, a column of fluid as light as air, 1222 feet high). But

air at 15° is lighter still than air at 0°, in the ratio 273 to 288, so that the air pressure measured in terms of air at 15° will be

$$1222 \times \frac{288}{273} = 1290 \text{ feet}$$

The velocity of the air supplied will therefore be, in feet per second:

$$V = \sqrt{64 \times 1290} \\ = 287 \text{ feet per second,}$$

and the volume delivered, per minute, at 15° C.:

$$287 \times 60 \times (0.7854 \times 9.5 \times 9.5 \div 144) \text{ cubic feet} \\ = 17,220 \times 0.492 = 8472 \text{ cubic feet,}$$

which in terms of air at 0° C., would be

$$847 \times \frac{273}{288} = 8050 \text{ cubic feet} \\ = 228 \text{ cubic meters}$$

The volume of waste gases produced in the 2 minutes can be found from the relative percentages of nitrogen in the air (79.2) and in the gases (78.6), as follows:

$$228 \times 2 \times \frac{79.2}{78.6} = 459.5 \text{ cubic meters}$$

Containing, therefore, from its analysis:

Carbon dioxide.....	82.25	cubic meters
Carbon monoxide.....	8.27	“ “
Oxygen.....	7.81	“ “
Nitrogen.....	<u>361.15</u>	“ “
	459.48	“ “

The carbon burnt to CO² and CO will be:

$$\begin{aligned} \text{C to CO}^2 & 82.25 \times 0.54 = 44.42 \text{ kilos.} \\ \text{C to CO} & 8.27 \times 0.54 = 4.47 \text{ “} \\ \text{Sum} & = 48.89 \text{ “} \end{aligned}$$

And the heat thus generated:

$$\begin{aligned} \text{C to CO}^2 & = 44.42 \times 8100 = 359,800 \text{ Calories} \\ \text{C to CO} & = 4.47 \times 2430 = 10,860 \text{ “} \\ \text{Sum} & = 370,660 \text{ “} \end{aligned}$$

To find the amount of this heat left in the producer at the end of the 2 minutes blowing up, we must subtract the $2 \times 9000 = 18,000$ Calories lost by radiation and conduction, and then, in addition, the heat carried out by the hot gases, at an average temperature of 900°C. , which latter will be:

$$\begin{array}{r} \text{CO, O}^2, \text{N}^2 \quad 377.25 \times 0.327 \times 885 = 109,150 \text{ Calories} \\ \text{CO}^2 \quad 82.25 \times 0.571 \times 885 = \quad 41,565 \quad \text{"} \\ \text{Sum} = \underline{150,715} \quad \text{"} \end{array}$$

Heat left in the fuel bed:

$$370,660 - 168,715 = 201,945 \text{ Calories}$$

heat capacity of the fuel bed per 1°C. :

$$\begin{array}{r} 3000 \times 0.9 \text{ kilos. carbon} \times 0.5 = 1370 \text{ Calories} \\ 3000 \times 0.1 \text{ kilos. ash} \quad \times 0.25 = \quad 75 \quad \text{"} \\ \text{Sum} = \underline{1445} \quad \text{"} \end{array}$$

Average rise in temperature of the fuel bed:

$$\frac{201,945}{1425} = 142^\circ \text{C.} \quad (1)$$

(2) The useful heat thus stored up in the fuel bed amounts to the following proportion of the total heat generated during the blowing up:

$$\frac{201,945}{370,660} = 0.545 = 54.5 \text{ per cent.} \quad (2)$$

(3) Steam which can be decomposed in the gas-producing period:

$$\begin{aligned} \frac{201,945}{2500} &= 80.8 \text{ kilograms} \\ &= 10.1 \text{ kilograms per minute} \end{aligned} \quad (3)$$

(4) Air supplied in 2 minutes = 456 cubic meters. Steam used in 8 minutes = 80.8 kilograms.

$$\begin{aligned} \text{Ratio} &= \frac{80.8}{456} = 0.177 \text{ kilos. steam per } 1 \text{ m}^3 \text{ air} \quad (4) \\ &= 0.177 \text{ ounce steam per } 1 \text{ ft}^3 \text{ air} \\ &= 1.1 \text{ pounds steam per } 100 \text{ ft}^3 \text{ air} \end{aligned}$$

CHAPTER VII.

CHIMNEY DRAFT AND FORCED DRAFT.

In all problems concerning combustion, we must furnish the air needed for combustion either by suction or by pressure. The original and almost universal method is by chimney draft; the more positive and reliable method is forced draft. Often the two are combined with very satisfactory results.

The waste heat from any metallurgical process or furnace is generally considerable. Most furnaces must be kept above a red heat, and the gases pass directly out of the furnace into the chimney. In such cases the chimney is indicated as the proper source of draft, because it utilizes, although very inefficiently, the ascensive force of the hot gases, and thus works by otherwise wasted energy. In other cases it is practicable to pass the gases through boilers before they go to the chimney, and thus to raise large amounts of steam. The gases are then cooled down so far that they enter the chimney too cold to furnish all the draft needed; in such cases a small fraction of the steam generated will run a steam engine or steam turbine, and run a fan capable of furnishing all the draft needed. In this manner considerable steam is available for other purposes, and great economy is effected.

CHIMNEY DRAFT.

The principles involved are not obscure or complicated. The total pull, or suction, which a chimney can produce, assuming it to be filled with hot air, is simply due to the ascensive force of the hot air inside, and the measure of this is the difference of weight of the chimney full of hot gases and what it would be if filled with cold air of the temperature outside.

Illustration: A chimney is 6 feet square inside and 100 feet high, uniform, with the gases inside at an average temperature of 500° F., and specific gravity (air = 1) of 1.06. The

air outside is at 80° F. What is the ascensive force of the hot gas inside, in total pounds, in ounces per square inch and inches of water gauge?

The volume of the space in the chimney—chimney volume—is $100 \times 6 \times 6 = 3600$ cubic feet. This volume, filled with air at 32° F., would weigh

$$3600 \times 1.293 = 4654.8 \text{ oz. av.} = 290.9 \text{ pounds.}$$

And, filled with gas at 500° F.,

$$290.9 \times 1.06 \times \frac{491}{500 - 32 + 491} = 157.9 \text{ pounds.}$$

If filled with outside air, at 80° F., the weight would be

$$290.9 \times \frac{491}{80 - 32 + 491} = 265.0 \text{ pounds.}$$

We, therefore, see that the hot gases in the chimney, weighing 157.9 pounds, displace 265.0 pounds of cold air, and the tendency of the former to rise upwards in this ocean of air must be

$$265.0 - 157.9 = 107.1 \text{ pounds.}$$

To put it in another way, if a piston fitted into the chimney at the bottom, and could move without friction, the piston would have to be loaded with 107.1 pounds to keep it from moving up the chimney. The total upward pull of the chimney is therefore 107.1 pounds.

Since this would be exerted on a piston $6 \times 6 = 36$ square feet in area, the pull or suction per square foot, in pounds, is $107.1 \div 36 = 2.98$ pounds, and in ounces per square inch.

$$(2.98 \div 144) \times 16 = 0.331 \text{ ounce per square inch.}$$

If the pull or suction is measured on a gauge, as by water pressure, the pressure of a 1-foot column of water at ordinary temperatures is 1000 ounces per square foot, or 1 inch of water is

$$(1000 \div 144) \div 12 = 0.597 \text{ ounces per square inch.}$$

The total pull of the chimney is therefore equivalent to

$$\frac{0.331}{0.579} = 0.57 \text{ inch of water gauge.}$$

By exactly similar methods of calculation the theoretical total suction of a chimney of any given height and temperature of gases inside and of air outside may be obtained. The suction expressed in ounces per square inch, or in water gauge is, of course, independent of the cross-sectional area of the chimney; it depends only on its height and on the temperatures inside and outside.

The above calculated total suction (allowing nothing for friction, etc.) is called the total head of the chimney, and is usually expressed in terms of cold air (at 0° C.) instead of in water. Cold air is a fluid, and water is 772 times as heavy as it; therefore, a gauge pressure or hydrostatic head of 0.57 inch of water is the same as

$$\begin{aligned} 0.57 \times 772 &= 440 \text{ inches of air.} \\ &= 36.5 \text{ feet of air.} \end{aligned}$$

What this head really represents is clearly seen from the above calculation. Its value is to be obtained directly from the height of the chimney, temperature inside and out and specific gravity of the chimney gases (air = 1) by the following relations, in which

h_0 = total head in feet of air at 32° F.

h_0 = total head in meters of air at 0° C.

t = temperature in the chimney, F°.

t = temperature in the chimney, C°.

t' = temperature of outside air, F°.

t' = temperature of outside air, C°.

D = Specific gravity of chimney gases, air = 1.

H = Height of chimney in feet.

H = Height of chimney in meters.

$$\text{coef} = \text{coefficient of gaseous expansion, F}^\circ = \frac{1}{491}$$

$$\text{coef} = \text{Coefficient of gaseous expansion, C}^\circ = \frac{1}{273} = \alpha$$

$$h_0 = H \left[\frac{(1-D + \text{coef} [(t-32) - D(t'-32)])}{[1 + \text{coef}(t'-32)] [1 + \text{coef}(t-32)]} \right]$$

$$h_0 = H \left[\frac{(1-D + \text{coef}(t-Dt'))}{(1+\alpha t')(1+\alpha t)} \right]$$

The author is not fond of using formulas whenever their use can be avoided. The above formulas express in the simplest mathematical form the principles which have been so far explained and used in the calculations, but it is strongly urged that the formulas be kept "for exhibition purposes only," and that when any specific case is to be worked it be attacked from the standpoint of the principles involved, as explained in the case worked. In other words, if one understands properly and thoroughly the basic principles, he has no need of the formula; if one does not understand the principles, the formula had better be kept forever in "innocuous desuetude."

The total head, obtained as above, is the theoretical head. It is like the pressure on the piston of a locomotive—the total available force for all purposes. Just as the pressure on the locomotive piston is used up in friction in the engine and in moving the engine itself, and the residue is the *available* pull on the draw-bar which moves the train, so the total head of the chimney is partly used up in friction in the chimney itself, partly in giving velocity to the gases as they pass out of the chimney, and the residue is the *available* head which draws or pulls the gases through fire-grates, furnaces and flues up to the base of the chimney. If the chimney could be momentarily completely closed at the bottom, except for the gauge opening, and the air inside be brought to rest, the gauge would show the total head; as soon as dampers are opened connecting the flues, air moves up the chimney, and the gauge pressure is lessened by the head required to move the gases and that absorbed in the friction in the chimney.

Head Represented in Velocity of Issuing Gases.—This item always exists when the chimney is working, and depends only on the velocity of the gases as they escape and their temperature. The hydraulic head necessary to give any fluid a velocity V is simply the same as the height which a falling body must fall in order to acquire that same velocity; *i.e.*:

$$h = \frac{V^2}{2g}$$

in which expression, $2g$ is the constant acceleration of gravity, 19.6 meters or 64.3 feet, and the velocity is in meters or feet per second. If we know, therefore, the velocity of the gases

issuing from the chimney, or can calculate or assume it, we can get h . In practice the velocity does not vary within very wide limits. In small house chimneys it may not exceed 3 feet per second, in boiler chimneys 6 to 12 feet per second, in furnace chimneys 12 to 20 feet per second. The temperatures of these issuing gases is, moreover

	C°	F°
In small chimneys.....	100 to 200	200 — 350
In boiler chimneys.....	100 to 300	200°— 550
In furnace chimneys.....	300 to 1000	550°—1800°

If the chimney in question has, therefore, a known velocity of exit of its gases, h can be calculated; but it must not be forgotten that h will be in terms of the kind of gases which is escaping; *i.e.*, of hot gas, and to subtract it from or compare it with h_0 we must reduce it to its equivalent head in terms of cold gas. This is merely a matter of taking into account the specific gravities or relative densities of hot gas and cold air, which are inversely proportional to their absolute temperatures; that is, if D represents the relative density of air and chimney gases at the same temperature:

$$h_0^{\text{vel.}} = h \times \frac{D}{1 + \alpha t} = \frac{V^2}{2g} \frac{D}{1 + \alpha t}$$

Illustration: Assuming the actual velocity of the gases issuing from a furnace chimney to be 15 feet per second, and their temperature 500° F., density 1.06 (air = 1), what will be the head represented by the velocity of these gases in terms of cold air at 32° F.?

The head represented, *in terms of hot gases* at 500° F., is

$$h = \frac{V^2}{2g} = \frac{15^2}{64.3} = 3.5 \text{ feet.}$$

In terms of air at 500° F. is

$$3.5 \times 1.06 = 3.71 \text{ feet.}$$

And in terms of air at 32° F.,

$$3.71 \times \frac{491}{500 - 32 + 491} = 1.9 \text{ feet.}$$

Out of the total head which this chimney produces (say 36.5 feet), 1.9 feet is represented by the velocity of the issuing gases, or 5.2 per cent. of the whole, leaving 34.6 feet to represent loss by friction in the chimney and the available head. We will proceed to discuss the loss of head due to friction in the chimney.

Head Lost in Friction in the Chimney.—This varies with the smoothness or roughness of the walls, and has been determined experimentally for air moving with different velocities. The manner of expressing the friction loss is, to put it as a function of the head necessary to give the gases their actual velocity, assuming there were no friction. Thus, supposing as in the preceding paragraph, the actual velocity of the hot gases is 15 feet per second, and the head (in terms of cold air) necessary to give that velocity, not considering friction, is 1.9 feet, then the head lost in friction in getting up this velocity will be

$$h_{\text{friction}} = 1.9 \times \frac{H}{d} K.$$

That is, it will be proportional to H , the height of the chimney, inversely as d , the diameter or side, if square, and to a coefficient K , determined by experiment. The latter varies, according to Grashof's experiments, between 0.05 for a smooth interior to 0.12 for a rough one, and averages 0.08.

Illustrations: Assuming the height of the chimney, 100 feet, its section to be 6 feet square, the coefficient of friction $K = 0.08$, and the head represented by the net velocity of the hot gases in the chimney to be 1.9 feet of cold air, what is the head lost in friction in the chimney?

The ratio of height to side is $100 \div 6 = 16.67$, which multiplied by K gives 1.33 as the value of the function containing these three terms. This means that 1.33 times as much head has been lost in friction as is represented by the net actual velocity of the gases as they pass up the chimney. Therefore,

$$h_{\text{friction}} = 1.9 \times 1.33 = 2.5 \text{ feet cold air.}$$

Another way of looking at this, which is sometimes useful in considering the height of a chimney, is to say

$$h_{\text{friction}} = 0.025 H.$$

Or, that in this case, the head lost in friction amounts numerically to one-fortieth the height of the chimney.

If we subtract the head lost in friction plus that represented in the net velocity of the gases, from the total gross head, the residue is that available for doing work external to the chimney. In the specific case of the preceding illustrations we have

h_0 = total head	= 36.5 feet = $\frac{100}{1}$ per cent.
h_{velocity} = velocity head	= 1.9 " = $\frac{5}{1}$ "
h_{friction} = friction in chimney	= 2.5 " = 7 "
$h_{\text{available}}$ = available head	= 32.1 " = 88 "

Available Head of a Chimney.—This is the part of the total head which remains after subtracting the head lost in friction in the chimney and that represented by the velocity of the issuing gases. In the specific cases considered in the above illustrations, the net available head amounted to 88 per cent. of the whole theoretical head. If we assume limiting conditions as found in practice, we can find the limiting values of this proportion. Calling the cases I and II, those with minimum and maximum absorption of head in the chimney itself, we have

	Case I.	Case II.
Temperature of issuing gases.....	100° C.	1000° C.
Velocity of issuing gases per second.....	1 meter	7 meters
Ratio H to d.....	10	50
Coefficient K.....	0.05	0.12
Specific gravity of gases (air = 1).....	1.00	1.06
Head as velocity of gases (meters of air)..	0.04 m.	0.56 m.
Head as velocity of gases (feet of air)....	0.13	1.87
Head absorbed in friction (meters of air)..	0.02	3.36
Head absorbed in friction (feet of air)....	0.07	11.2
Head used up in chimney (meters).....	0.06 to	3.92
Head used up in chimney (feet).....	0.20 to	13.0
Water gauge pressure thus lost, m.m.....	0.1 to	5.0
Water gauge pressure thus lost, inches....	0.003 to	0.2

The available head, will, therefore, be the theoretical total head minus a loss in the chimney itself, which may amount to a maximum of 3.9 meters or 13 feet, representing an absorption of water gauge pressure up to 5 millimeters, or 0.2

inch at a maximum. Under ordinary conditions half these quantities would be a rather high chimney loss.

In most conditions which confront the metallurgist, the question is to determine how high a chimney should be built in order to supply a certain available draft determined by practice to be necessary. For instance, to burn a certain amount of coal per hour on any grate requires a certain amount of draft. This amount is increased if the draft is increased, and *vice versa*. In boilers, 18 pounds of coal burned per square foot of grate surface per hour is highly economical practice, and requires a draft of 0.4 inch to 0.8 inch of water gauge, according to the kind of coal burned. In furnaces where the amount of coal burned is greater per hour there will be usually a correspondingly greater temperature in the chimney. To calculate the height of chimney required it is necessary to assume only the temperature in the chimney, the available draft required and an average chimney loss.

Problem 22.

It is desired to design a chimney for a puddling furnace, the grate of which is 4 feet by 6 feet, and which shall burn 30 pounds of bituminous coal per hour per square foot of grate surface. Temperature of gases entering the chimney 1200° C., at the top probably 1000° C. Specific gravity of gases 1.03 (air = 1). Draft required 0.6 inch of water gauge. Outside temperature 30° C.

Solution: We can assume that since the gases will be at an average temperature of 1100° C. in the chimney, their velocity will be high, and that at least 0.1 inch of water gauge pressure will be absorbed by the chimney itself. This makes a total requirement of 0.7 inches of water for total head, or

$$h_0 = 0.7 \times 772 \div 12 = 45 \text{ feet of cold air.}$$

Or an unbalanced pressure or ascensive force of

$$45 \times 1.293 \div 16 = 3.64 \text{ pounds per square foot.}$$

Considering the air outside the chimney, its weight at 30° C. is equal, per cubic foot,

$$1.293 \times \frac{273}{303} \div 16 = 0.073 \text{ pounds.}$$

The gases inside the chimney weigh, per cubic foot,

$$1.293 \times 1.03 \times \frac{273}{1100 + 273} \div 16 = 0.0166 \text{ pounds.}$$

The height of the chimney being called H and its cross-section S, the volume is $H \times S$, and the weight of hot air inside it is

$$(H \times S) \times 0.0166 \text{ pounds.}$$

And of an equal volume of cold air outside

$$(H \times S) \times 0.073 \text{ pounds,}$$

giving a total ascensive force of

$$(H \times S) \times 0.0564 \text{ pounds.}$$

But there is needed a total ascensive force of

$$S \times 3.64 \text{ pounds,}$$

in order to give the pull of 3.64 pounds per square foot, and, therefore, of necessity,

$$H \times S \times 0.0564 = S \times 3.64,$$

from which

$$H = \frac{3.64}{0.0564} = 64.5 \text{ feet.}$$

Concerning the cross-section of this chimney, it would not be safe to make it less in diameter than one-fiftieth of its height, because of lack of stability; in fact, one-twenty-fifth would be better practice. This consideration would make its internal diameter 2 ft. 7 inches, area 5.2 square feet. Another way of arriving at a diameter is to calculate the volume of the hot gases which must pass up the chimney and assume for them some maximum velocity in the chimney, such as, let us say, 6 meters (20 feet) per second, and so get the minimum area necessary for filling this condition as follows:

Coal burnt per hour $4 \times 6 \times 30$	=	720 pounds.
Air theoretically necessary, assuming average bituminous coal (see Prob. 1)	=	123
$\times 720$	=	88.560 cubic feet

Products of combustion at standard conditions = 129×720	=	92,880 cubic feet
Volume chimney gases at 1100°C .	=	
$92,880 \times \frac{1700 + 273}{273}$	=	467,100 "
Volume per second	=	130 "
Area of chimney, if maximum velocity is 20 feet per second	=	6.5 sq. feet
Diameter, if round	=	2 ft. 10 in.

This chimney would do its work better, and there would be much less loss in friction, if the internal diameter were made 25 per cent. greater than the above calculated minimum, say, therefore, 3 feet 6 inches, making the area nearly 50 per cent. greater and cutting down the velocity in the chimney to 13.5 feet per second.

Problem 23.

In the case of the puddling furnace of Problem 19, assume that the hot gases, instead of going directly into the chimney, are passed through the flues of a boiler placed above the furnace, and thence pass into the chimney at a point 15 feet higher than before. Assume chimney 3 feet 6 inches internal diameter, 64.5 feet high above the furnace flue, and that the gases now passing into it 15 feet higher up are at 350°C ., and cool to 250°C . at the top of the chimney. The boiler flues introduce additional frictional resistance equal to 0.1 inch of water. The boiler raises steam at a net efficiency of 45 per cent., the steam engine utilizes the steam at a mechanical efficiency of 20 per cent., and a centrifugal fan supplies the forced draft needed at a mechanical efficiency of 25 per cent.

Required: (1) The total head of the chimney, when the furnace discharged directly into it, and the average temperature of the gases in it was 1100°C ., and specific gravity 1.03 (air = 1).

(2) The head absorbed as velocity of the outgoing gases, their temperature being 1000°C .

(3) The head lost in friction in the chimney, in this case.

(4) The head which was available to run the puddling furnace.

(5) The total head of the chimney with the gases entering 15 feet above former flue, and average temperature 300°C .

(6) The head absorbed in this case as velocity of outgoing gases, their temperature being 250° C.

(7) The head lost in friction in the chimney in this case.

(8) The available head to draw gases into the chimney.

(9) The deficit of head which must be made up by forced blast under the grate of puddling furnace.

(10) The horse-power absorbed by the fan which furnishes this blast.

(11) The horse-power furnished by the engine using the steam from the boiler.

(12) The excess of power which is thus saved and available for other purposes.

Solution:

(1) Volume of gases in chimney:

$$64.5 \times 3.5 \times 3.5 \times 0.7854 = 620.5 \text{ cu. ft.}$$

Weight at 32° F. (0° C.):

$$620.5 \times (1.293 \div 16) \times 1.03 = 51.65 \text{ lbs.}$$

Weight if temperature is 1100° C.:

$$51.65 \times \frac{273}{1100 + 273} = 10.27 \text{ lbs.}$$

Weight of equal volume of air outside at 30° C.:

$$620.5 \times (1.293 \div 16) \times \frac{273}{30 + 273} = 45.18 \text{ lbs}$$

Difference of weight = ascensive force,

$$45.18 - 10.27 = 34.91 \text{ lbs.}$$

Ascensive force per square foot,

$$34.91 \div 9.62 = 3.63 \text{ lbs.}$$

Total head in terms of cold air at 0° C.,

$$3.63 \div (1.293 \div 16) = 44.9 \text{ ft.} \quad (1)$$

In terms of water gauge pressure,

$$44.9 \times 12 \div 772 = 0.685 \text{ ins.} \quad (1)$$

- (2) Volume of gases per hour at 0° C.,
(Prob. 22) = 92,880 cu. ft.

Volume at 1000° C.,

$$= 92,880 \times \frac{1000 + 273}{273} = 433,100 \text{ cu. ft.}$$

Velocity per second,

$$433,100 \div (3600) \div 9.62 = 12.50 \text{ ft.}$$

Head necessary to give this velocity, in terms of hot gases,
at 1000° = $(12.50)^2 \div 64.3$ (2g) = 2.43 ft.

In terms of gases at 0° C.,

$$2.43 \times \frac{273}{1000 + 273} = 0.52 \text{ ft.}$$

In terms of air at 0° C.,

$$0.52 \times 1.03 = 0.55 \text{ ft.} \quad (2)$$

In terms of water gauge pressure,

$$0.55 \times 12 \div 772 = 0.008 \text{ in.} \quad (2)$$

- (3) Assuming K, the coefficient of friction, 0.08, then

$$h_0 \text{ friction} = \frac{V^2}{2g} \frac{273}{273 + t} \frac{H}{d} K. D.$$

This is only an abbreviated form of the operations done under (2), adding the terms which account for the height, diameter and friction. Now, the velocity per second:

$$V = 92,880 \times \frac{1100 + 273}{273} \div 3600 \div 9.62 = 13.5 \text{ ft}$$

Head necessary to give this velocity in terms of air at 0°,

$$(13.5)^2 \div 64.3 \times \frac{273}{273 + 1100} \times 1.03 = 0.58 \text{ ft.}$$

Proportion of this velocity head lost in friction =

$$\frac{H}{d} K = \frac{64.5}{3.5} \times 0.08 = 1.47$$

Head lost in friction in chimney,

$$0.58 \div 1.47 = 0.85 \text{ ft.} \quad (3)$$

In terms of water gauge pressure,

$$0.85 \times 12 \div 772 = 0.013 \text{ in.} \quad (3)$$

(4)	<i>Cold Air.</i>	<i>Water Gauge.</i>
Total head.....	44.90 feet	0.685 inch
Absorbed in velocity of gases.....	0.55 "	0.008 "
Absorbed in friction in chimney....	0.85 "	0.013 "
Available for the furnace.....	<u>43.50</u> "	<u>0.664</u> " (4)

(5) Volume of chimney gases,

$$(64.5 - 15) \times 3.5 \times 3.5 \times 0.7854 = 475.7 \text{ cu. ft.}$$

Weight at 300° C., specific gravity 1.03 (air = 1).

$$475.7 \times (1.293 \div 16) \times 1.03 \times \frac{273}{273 + 300} = 18.86 \text{ lbs.}$$

Weight of equal volume of outside air at 30° C.,

$$475.7 \times (1.293 \div 16) \times \frac{273}{273 + 30} = 34.68 \text{ lbs.}$$

Ascensive force of air per square foot,

$$(34.68 - 18.86) \div 9.62 = 1.64 \text{ lbs.}$$

Total head in terms of cold air,

$$1.64 \div (1.293 \div 16) = 20.3 \text{ ft.} \quad (5)$$

In terms of water gauge pressure,

$$20.3 \times 12 \div 772 = 0.32 \text{ in.} \quad (5)$$

(6) Velocity of issuing gases, per second, at 250° C.,

$$92,880 \times \frac{250 + 273}{273} \div 3,600 \div 9.62 = 5.14 \text{ ft.}$$

Head as velocity in terms of cold air at 0° C.,

$$(5.14)^2 \div 64.3 \times \frac{273}{273 + 250} \times 1.03 = 0.22 \text{ ft.}$$

In terms of water gauge pressure = 0.003 in.

(7) Average velocity of gases in chimney at 300° C.,

$$92,880 \div 3,600 \times \frac{300 + 273}{273} \div 9.62 = 5.63 \text{ ft.}$$

Head lost in friction in terms of cold air,

$$(5.63)^2 \div 64.3 \times \frac{273}{300+273} \times 1.03 \times \frac{49.5}{3.5} \times 0.08 = 0.27 \text{ ft.} \quad (7)$$

In terms of water gauge pressure = 0.004 in. (7)

(8)	<i>Cold Air.</i>	<i>Water Gauge.</i>	
Total head.....	20.30 feet	0.320 inch	
Absorbed in velocity of gases.....	0.22 "	0.003 "	
Absorbed in friction in chimney....	0.27 "	0.004 "	
Available to draw gases in.....	19.81 "	0.313 "	(8)

(9)

Available head needed for puddling

(4).....	43.50 "	0.664 "
Available head needed for boiler....	6.43 "	0.100 "
Total head needed for both.....	46.93 "	0.746 "
Available head from chimney (8)...	19.81 "	0.313 "
Deficit. to be supplied by blast....	27.12 "	0.451 "

(10) The 0.451 inches of water gauge equals

$$(0.451 \div 12) \times 62.5 = 2.35 \text{ lbs. per sq. ft.}$$

The volume of air to be supplied is, at 30° C.,

$$88,560 \text{ (Prob. 19)} \div 60 \times \frac{273+30}{273} = 1,638 \text{ cu. ft. per min.}$$

Net work done by the fan,

$$1,638 \times 2.35 = 3,850 \text{ ft. lbs. per min.}$$

Gross power needed by the fan,

$$3,850 \div 0.25 \text{ (efficiency)} = 15,400 \text{ ft. lb. per min.}$$

Horse-power needed to drive the fan,

$$15,400 \div 33,000 = 0.47 \text{ H. P.} \quad (10)$$

(11) The boiler receives the gases at 1200° C. and discharges them at 350°, and 92.880 cubic feet of gases (measured at standard conditions) pass through per hour. The composition of these gases is not given, but from the specific gravity we might conclude that they contain on an average 10 per cent. of carbon dioxide, since if they contained the maximum amount

of that gas (about 20 per cent.) their specific gravity would be 1.06 (air=1). Assuming them, therefore, to contain

CO ²	10 per cent.
H ² O.....	10 “
CO, N ² , O ²	80 “

their heat capacity per degree per cubic foot would be, between 350° and 1200°.

$$\text{CO}^2 \quad 0.1 \times [0.37 + 0.00022 (350 + 1200)] = 0.0711 \text{ oz. cal.}$$

$$\text{H}^2\text{O} \quad 0.1 \times [0.34 + 0.00015 (350 + 1200)] = 0.0573 \text{ “}$$

$$\text{CO, N}^2, \text{O}^2 \quad 0.9 \times [0.303 + 0.000027(350 + 1200)] = 0.0310 \text{ “}$$

$$\text{Sum} = 0.1594 \text{ “}$$

Heat given up per cubic foot,

$$0.1594 \times (1200 - 350) = 125.5 \text{ oz. cal.}$$

Heat given up by gases per hour to boiler,

$$92,880 \times 125.5 = 11,656,500 \text{ oz. cal.}$$

$$= 728,500 \text{ lb. cal.}$$

Heat in the steam produced per hour,

$$728,500 \times 0.45 \text{ (efficiency)} = 327,800 \text{ lb. cal.}$$

Heat equivalent of mechanical energy of steam engine per hour,

$$327,800 \times 0.20 \text{ (efficiency)} = 65,560 \text{ lb. cal.}$$

$$\text{Heat equivalent of 1 hp hour} = 635 \text{ kg. cal.}$$

$$= 1,400 \text{ lb. cal.}$$

Horse-power generated by the engine,

$$65,560 \div 1,400 = 46.8 \text{ H. P.} \quad (11)$$

(12) Net available power after supplying fan,

$$46.8 - 0.5 = 46.3 \text{ H. P.} \quad (12)$$

CHAPTER VIII.

CONDUCTION AND RADIATION OF HEAT.

These two factors are of the greatest practical importance to the metallurgist, yet they are also the subjects of all others upon which the practical metallurgist is usually the most poorly informed. It often happens that a furnace is built of twice the capacity of its predecessor or of its neighbors, and the manager unexpectedly and most agreeably discovers that it keeps up a more uniform heat and requires considerably less than twice the amount of fuel to keep it running. Two reasons were operative; first, the walls were made thicker to support the heavier structure, but that made them also poorer conductors of heat; second, the capacity increased as the cube of a linear dimension, while the radiating surface increased as its square, so that radiation was, therefore, less than twice the primary amount from the furnace of double capacity. Many practical metallurgists have learned the practical results, but are entirely ignorant of the principles upon which the results are obtained. While it is well to be successful, it is better to be intelligently so.

PRINCIPLES OF HEAT CONDUCTION.

It is well known that the ability of metals to conduct heat is very nearly the same as their ability to conduct electricity. The order of metals in these two series is almost identical. Further, the specific conductance for heat is closely analogous to specific conductance for electricity. Just as we say that the electrical resistance of a conductor is proportional to its length and inversely as its cross-section, so we can make the same statement concerning heat resistance. Just as we can add electrical *resistances* when the bodies are in series, and must add electrical *conductances* when they are in parallel, so we

can add heat resistances when the bodies are in line, and must add heat conductances when they are hooked up together in parallel.

The unit of electrical resistance is an ohm, and a substance has unit resistivity when a cube of it, 1 centimeter on a side, has that resistance. In such a case a drop of potential of 1 volt from one side to the opposite one sends through the cube 1 coulomb of electricity per second. Since conductivity is merely the reciprocal quality, actually and mathematically, to resistivity, the unit of conductivity is defined in exactly the same way, and the conductivity of any substance may be expressed as so many reciprocal ohms.

If we read in the preceding paragraph, thermal resistance for electrical resistance, degrees temperature for volts, and gram calories for coulombs, we have defined the corresponding unit of thermal resistivity. A substance has unit capacity for conducting heat when a cube 1 centimeter on a side transmits 1 gram calorie of heat per second, with a drop of temperature from one surface to the other of 1° C. Many investigators have adopted slightly different units, such as 1-kilogram Calorie per cubic meter per hour per degree difference; but such are only simple multiples or fractions of the centimeter-gram-second unit above defined.

Illustration: If the thermal conductivity of copper is 0.92 units, what would be the amount of heat passing per hour through a sheet 1 millimeter thick and 1 meter square, with a constant difference of 1° C. between the two sides?

Solution: The 0.92 units means that a column of copper 1 centimeter long and 1 square centimeter in cross-section, having a difference of temperature at its two surfaces of 1° C., would allow 0.92 gram-calories of heat to flow through it per second. For a sheet one-tenth as thick, 10,000 times the area and during 1 hour, the heat passing per 1° C. difference will be

$$\begin{aligned} 0.92 \times \frac{10}{1} \times \frac{10,000}{1} \times 3600 &= 331,200,000 \text{ cal.} \\ &= 331,200 \text{ Cal.} \end{aligned}$$

Such calculations as the above are, of course, very useful for comparing different thicknesses of plates of different material, as to their relative heat-carrying capacity. With some slight

modifications they are applicable to the actual conveyance of heat through such walls, from a fluid on one side to a fluid on the other. This introduces an idea analogous to transfer or contact resistance in electrolytic conduction. Thus, if we call R the thermal specific resistance (resistivity) in C. G. S. units, of the material of a partition having a thickness of d centimeters, and an area of S square centimeters, then the thermal resistance of the body of the partition will be

$$\frac{R \times d}{S}$$

and its thermal conductivity

$$\frac{S}{R \times d} = k$$

Besides this resistance in the body of the material there is transfer resistance at its two sides, or at its inner and outer surfaces, which depends on the materials which communicate heat and receive heat, and their velocity. These resistances may be expressed as so many units per square centimeter, the unit being of exactly the same nature as R , except that it connotes no thickness but merely a surface effect. Calling R^1 the specific resistance of transfer from the inner fluid to the inner surface of the material, and R^2 the outside specific transfer resistance to the fluid outside, we can consider all three resistances as being in series, and the total thermal resistance to transfer from the inside fluid to the outside fluid to be

$$\frac{R \times d}{S} + \frac{R^1}{S} + \frac{R^2}{S}$$

or the thermal conductance of the system

$$\frac{S}{(R \times d) + R^1 + R^2} = k$$

The following table gives the thermal resistivity of various materials, in C. G. S. gram-Calorie units, also the thermal conductivity in units which are reciprocals of the resistance units:

<i>Material.</i>	<i>Conductivity (in reciprocal resistance units.)</i>	<i>Resistivity (in C. G. S. gram-cal. units.)</i>
Silver (at 0°).....	1.10	0.91
Copper (0°—30°).....	0.92	1.09
Copper, commercial.....	0.82	1.22
Copper, phosphorized.....	0.72	1.39
Magnesium.....	0.38	2.63
Aluminium (0°).....	0.34	2.94
Aluminium (100°).....	0.36	2.75
Zinc (15°).....	0.30	3.33
Brass, yellow (0°).....	0.20	5.00
Brass, yellow (100°).....	0.25	4.00
Brass, red (0°).....	0.25	4.00
Brass, red (100°).....	0.28	3.57
Cadmium (0°).....	0.20	5.00
Tin (15°).....	0.15	6.67
Iron, wrought (0°).....	0.21	4.76
Iron, wrought (100°).....	0.16	6.25
Iron, wrought (200°).....	0.14	7.14
Iron, steel, soft.....	0.11	9.01
Iron, steel, hard.....	0.06	16.67
German silver (0°).....	0.07	14.28
German silver (100°).....	0.09	11.11
Lead (0°).....	0.084	11.90
Lead (100°).....	0.076	13.16
Antimony (0°).....	0.044	22.73
Mercury (0°).....	0.015	66.67
Mercury (50°).....	0.019	52.63
Mercury (100°).....	0.024	41.67
Bismuth (0°).....	0.018	55.55
Wood's alloy (7°).....	0.032	31.25
Alloy, 1 Sn. 99 Bi.....	0.008	125.00

The last alloy, bismuth, with only 1 per cent. of tin, is remarkable for its extremely low heat conductivity, less than one hundredth as good as copper. It has also the lowest electrical conductivity of any alloy, about one two hundredth that of copper. These peculiar properties ought to make it of use for some particular purposes.

The above data enables one to calculate the rate at which heat

will pass through a metallic partition or wall when the temperature of its two surfaces is known. This is a very useful calculation, for in many cases the temperature inside a partition or pipe is known, or can be easily determined, and when the temperature of the outside surface is determined, the calculation can be made. The temperature of the outside of a partition or pipe can be found by several methods: one is to lay a very flat bulb thermometer (made especially for this purpose) against it; another is to put the junction of a thermocouple against it, covering the couple with a little putty or clay; another is to take small pieces of metals, or alloys of known melting points, and see which melts against the hot metal. The only uncertainty then in the calculation is the question as to what difference in the conductivity may be caused by the higher temperature. The conductivities in most cases decrease as temperature rises, but in others increase. There is here a large field for metallurgical experiment, in determining the heat conductivities of metals, alloys and fire-resisting materials at high temperature.

Illustration: An iron pipe, 6 centimeters in diameter outside and 5 centimeters inside, is filled with water at 10° C., and surrounded by hot gases at 198° C. From the rise in temperature of the water it is known that for each square centimeter of heating surface 0.084-gram calories of heat pass per second. Assuming the thermal conductivity of the iron (k) = 0.14, what is the difference of temperature of the two surfaces, inside and outside, of the pipe?

Solution: The thickness of the walls is $(6-5) \div 2 = 0.5$ centimeter. If the walls were 1 centimeter thick, 1° difference would transmit 0.14 calorie; but being only half that thick, 1° difference would transmit 0.28-gram calorie. The actual difference of temperature of the two surfaces must then be

$$\frac{0.084}{0.28} = 0.3^{\circ} \text{ C.}$$

Of course, such calculations can be turned around, and if the temperature of the inside and outside surfaces is known, the heat being transmitted can be calculated; or if the temperature of these two surfaces is known and the heat being transmitted is measured, the thermal conductivity of the partition can be

reckoned; or, again, if the temperature of the two surfaces is known, and also the thermal conductivity of the partition, and the temperature of either fluid on either side, the thermal resistance of the transfer from either of the fluids to the surface of the partition can be calculated.

Illustration; In the previous illustration the temperature of the hot gases was 198° , while that of the pipe in contact with them was practically 10° . What was the thermal resistivity of the transfer from gas to metal?

Solution: The thermal resistivity is the reciprocal of the thermal conductivity, and in the case of this transfer resistance is the reciprocal of the number of gram calories which will be transferred to 1 square centimeter of pipe surface from the hot gases per second per each degree centigrade of difference of temperature causing the flow. This is a surface or skin resistance, and, therefore, no linear dimension representing thickness enters into the calculation. There is 0.084 calorie per second being transferred to each square centimeter of pipe, with a difference of temperature acting as propelling force of $198 - 10 = 188^{\circ}$. The thermal conductivity of this transfer, k , is, therefore,

$$0.084 \div 188 = 0.00045$$

And the thermal resistivity, R , the reciprocal, viz.: 2222. Since the thermal resistivity of the iron wall is $1 \div 0.28 = 3.57$ units, it follows that the contact surface offers $2222 \div 3.57 = 622$ times as much resistance to the flow of heat as the metal itself. In this specific instance, we can conclude that the transfer of heat from the gases to the pipe is the principal item which conditions the flow of heat, the passage of the heat through the wall of the pipe itself taking place 622 times as readily.

The valuable practical conclusion is that the thermal resistance of the walls of the pipe is insignificant as compared with the whole thermal resistance, and the thickening or thinning of the walls of the pipe, or the substitution of copper for iron, because of its greater thermal conductivity, is practically unnecessary for thermal considerations, since such can be expected to make practically no change in the thermal resistance of the whole system.

If the pipe under discussion, however, acquires during use a

layer of scale deposited from the water, then the thermal resistance of the pipe or of the system is materially affected. A study of the thermal resistivity of various boiler scales would be a very useful and practical subject, but has not been done, as far as the writer is aware. Assuming a deposit, 0.5 centimeter thick, of material having the thermal conductivity of plaster of paris, for which $k = 0.0013$, the specific resistance of this material is $0.14 \div 0.0013 = 108$ times that of iron, and therefore 0.5 centimeter of this represents 54 centimeters thickness of iron. The thermal resistances in this case, neglecting that of transfer from the water to the pipe or scale, are as follows:

Resistance of transfer, gases to pipe = 2222.0 = 85 per cent.

$$\text{Resistance of 0.5 c.m. iron} = \frac{0.5}{0.14} = 3.6 = 0 \quad "$$

$$\text{Resistance of 0.5 c.m. scale} = \frac{0.5}{0.0013} = 384.4 = 15 \quad "$$

$$\text{Total} = \overline{2610.0}$$

It thus appears that a deposit of scale from the water to a thickness of 5 millimeters increases the total thermal resistance of the system some 18 per cent. of its original amount, and would cut down the efficiency of this part of the heating surface of a boiler by this amount. These considerations are not only of vital importance to the steam boiler engineer, but they are the essential principles which condition the efficiency of steam-heating apparatus, feed-water heaters, hot-air stoves and ovens, air-cooling of parts of furnaces and the efficiency of water jackets.

PRINCIPLES OF HEAT TRANSFER.

We have already had to speak of the transfer of heat from fluids to solids, or *vice versa*, and in one specific case we deduced the value 2222 for the transfer resistivity from hot gases to the surface of iron pipe, meaning thereby that for each degree of temperature difference between the gases and outside of the pipe 0.00045 gram calorie passed per second through each square centimeter of contact surface. A consideration of the transfer of heat through such contact surfaces, from gases or liquids to solids and *vice versa*, has shown that the

transfer resistivity varies with the solid and with the fluid concerned, but much more with the latter than with the former, and is very largely dependent upon the circulation of the fluid, that is, upon the rate at which it is renewed, and therefore upon its velocity. The conductivity or resistivity of such a transfer must, therefore, contain a term which includes the velocity of the fluid. Various tests by physicists have shown the specific conductance (or conductivity of transfer) to vary approximately as the square root of the velocity of the fluid.

From metal to air or similar gases, the mean velocity of flow being expressed in centimeters per second, and the other units being square centimeters and gram calories, the transfer resistivity is approximately

$$R = \frac{36,000}{2 + \sqrt{v}}$$

and the transfer conductivity of the contact

$$k = 0.000028 (2 + \sqrt{v})$$

From hot water to metal the relations are similar, but the conductivity is much better. Experiments show values as follows:

$$k = 0.000028 (300 + 180\sqrt{v})$$

$$R = \frac{36,000}{300 + 180\sqrt{v}}$$

Illustration: In the preceding case of the iron pipe, calculate the difference of temperature of the water in the pipe and the inner surface of the pipe, assuming the water to be passing through at a velocity of 4 centimeters per second.

Using the above given formula, the heat transfer per 1° difference would be

$$0.000028 (300 + 180\sqrt{4}) = 0.0185 \text{ calories,}$$

and the difference to transfer 0.084 calories per second will be

$$\frac{0.084}{0.0185} = 4.6$$

The inner surface of the iron pipe will be, therefore, continuously 4.6 higher than the water, and, therefore, at 14°.6;

the outer surface will be continuously $0^{\circ}.3$ higher, or practically at 15° .

Illustration: A steam radiator, surface at about 100° C., caused a current of hot air to rise having a velocity of about 10 centimeters per second, which was insufficient to keep the room warm. An electric fan was set to blow air against the radiator, which it did with a velocity of about 300 c.m. per second, and keeping the room comfortably warm. What were the relative quantities of heat taken from the radiator in the two cases?

The relative thermal conductivities of transfer were

$$2 + \sqrt{10} : 2 + \sqrt{300}$$

or

$$5 : 16$$

Showing over three times as much heat taken away per unit of time in the second instance.

This illustration proves the great efficiency which the metallurgist may attain in air cooling of exposed surfaces, by blowing the air against them instead of merely allowing it to be drawn away by its ascensive force.

Problem 24.

Hot air of the volume of 33,000 cubic meters per hour passes through an iron pipe exposed to the air, 30 meters long, 1.5 meters inside diameter, thickness of walls 1 centimeter, and lined inside with 5 centimeters of fire-brick. Assume the hot air entering at $1,000^{\circ}$, the outside air to be at 3° , the coefficient of internal transfer $0.000028 (2 + \sqrt{v})$, the conductivity of the fire-bricks 0.0014, of the iron 0.14, of external transfer $0.000028 (2 + \sqrt{v})$, the velocity of the wind against the outside 6 kilometers per hour.

Required: The temperature of the hot air leaving the tube.

Solution: The mean temperature in the tube is the factor which conditions the mean velocity in the tube, and the rate of flow of heat towards the outside. If, therefore, we let t represent that mean temperature, the solution can be stated in the simplest terms. We then have:

Volume of air per hour, at 0° , = 33,000 cubic m.

Volume of air per second, at 0° , = 9.167 "

$$\text{Volume of air per second, at } t, = 9.167 \frac{t+273}{273}$$

Cross-section of inside of tube

$$(1.5-0.1)^2 \times 0.7854 = 1.54 \text{ sq. m.}$$

Velocity of air at t , in pipe

$$9.167 \frac{t+273}{273} \div 1.54 = 5.95 \left(\frac{t+273}{273} \right) \text{ m. p. s.}$$

$$= 5.95 (1 + \alpha t) \text{ m. p. s.}$$

$$= 595 (1 + \alpha t) \text{ c.m. p. s.}$$

Coefficient of internal transfer =

$$0.000028 (2 + \sqrt{595 (1 + \alpha t)})$$

Coefficient of conductance of 5 c.m. of fire-brick lining =

$$0.0014 \div 5 = 0.00028$$

Coefficient of conductance of 1 c.m. of iron =

$$0.14 \div 1 = 0.14$$

Coefficient of external conductance ($v = 278$ c.m. per sec.) =

$$0.000028 (2 + \sqrt{278}) = 0.000515$$

Total fall of temperature of air = $2 (1000 - t)$

End temperature of the air = $1000 - 2 (1000 - t)$

$$= 2t - 1000$$

Mean specific heat of air per cubic meter between 1000 and end temperature =

$$0.303 + 0.000027 (2t)$$

Heat given out by the air per hour =

$$33,000 \times 2(1000 - t) \times (0.303 + 0.000027 (2t)) =$$

$$19,998,000 - 16,414 t - 3.564 t^2$$

This heat is the quantity transferred through the pipe in kilogram Calories. The outside surface of the pipe may be taken as the conducting surface, because the larger part of the resistance to the flow of heat takes place there. If we desired to be more exact, the mean area of iron, fire-bricks and the inner surface could be each used separately. The outside diameter being 150 centimeters, and the length 30 meters, the outer surface is $1.52 \times 3.1416 \times 30 = 142.3$ square meters = 1,423,000 square centimeters, the total driving force is the inside temperature minus that outside, or $t - 3$, and the total

thermal resistance is the sum of the four thermal resistances in series, that is, the sum of thermal resistance gas to fire-bricks =

$$\frac{1}{0.000028 (2 + \sqrt{595 (1 + \alpha t)})}$$

thermal resistance of fire-brick lining =

$$\frac{1}{0.00028}$$

thermal resistance of iron shell =

$$\frac{1}{0.14}$$

thermal resistance of iron to air =

$$\frac{1}{0.000515}$$

The reciprocal of the sum of these four resistances is the thermal conductance of the system per square centimeter, which, multiplied by the conducting surface, 1,423,000 square c.m., and by the total difference of temperature, $t-3$, gives the heat transferred per second in gram calories.

We, therefore, have the final equality expressed as the heat given up by the air, per second, equals the heat transmitted to the outside air per second; *i.e.*,

$$\frac{1000}{3600} (19,998,000 - 16.414 t - 3.564 t^2) =$$

$$\frac{1}{\frac{1}{0.000028 (2 + \sqrt{595 (1 + \alpha t)})} + \frac{1}{0.00028} + \frac{1}{0.14} + \frac{1}{0.000515}} \times 1,423,000 \times (t-3)$$

Whence $t = 965^{\circ}.5$

And the temperature of the air at the end of the tube is

$$2t - 1000 = 931^{\circ} \quad (1)$$

It would be interesting to compare the temperatures of the inside and outer surfaces of the tube. The air inside is at a mean temperature of 965° , the heat transmitted per second is 0.1574-gram Calories per square centimeter of outer surface,

whose thermal conductivity is 0.000515, and therefore, the outside surface must be

$$\frac{0.1574}{0.000515} = 306^{\circ}$$

hotter than the surrounding air; that is, must be at 309° C.

The extra loss of heat by radiation from this outside surface would be small at that low temperature, but has not been allowed for in the working of the problem.

For such metallurgical problems we need the data as to the thermal conductivity or resistivity of ordinary furnace materials. These have been determined in but few instances, and in most cases not at the high temperatures at which they are practically used. A whole series of physico-metallurgical experiments is needed just upon this point. The following are probably nearly all that have been determined and the values published. The unit *k* is the C. G. S.-gram calories unit, the same as used for the metals.

k.

Ice (datum useful in refrigerating plants, where pipes become coated with ice, as in Gayley's method of drying blast).....	0.00500
Snow.....	0.00050
Glass (10°—15°).....	0.00150
Water.....	0.00120
Quartz sand (18°—98°).....	0.00060
Carborundum sand (18°—98°).....	0.00050
Silicate enamel (20°—98°).....	0.00040
(Explains the small conductance of enameled iron ware.)	
Fire-brick, dust (20°—98°).....	0.00028
Retort graphite dust (20°—100°).....	0.00040
(Datum useful where articles are packed in this poorly conducting material.)	
Lime (20°—98°).....	0.00029
(Datum would be highly useful for oxyhydrogen platinum furnaces, if it were only known at high temperatures.)	
Magnesia brick, dust (20°—100°).....	0.00050
Magnesia calcined, Grecian, granular (20°—100°).....	0.00045
Masonry	0.0036 to 0.0058
Water, uncirculated	0.0012 to 0.0016

Magnesia calcined, Styrian, granular (20°—100°).....	0.00034
Magnesia calcined, light, porous (20°—100°).....	0.00016
Infusorial earth (Kieselguhr) (17°—98°).....	0.00013
Infusorial earth (0°—650°).....	0.00038
Clinker, in small grains (0°—700°).....	0.00110
Coarse ordinary brick dust (0°—100°).....	0.00039
Chalk (0°—100°).....	0.00028
Wood ashes (0°—100°).....	0.00017
Powdered charcoal (0°—100°).....	0.00022
Powdered coke (0°—100°).....	0.00044
Gas retort carbon, solid (0°—100°).....	0.01477
Cement (0°—700°).....	0.00017
Alumina bricks (0°—700°).....	0.00204
Magnesia bricks (0°—1300°).....	0.00620
Fire-bricks (0°—1300°).....	0.00310
Fire-bricks (0°—500°).....	0.00140
Marble, white (0°).....	0.0017
Pumice.....	0.0006
Plaster of paris.....	0.0013
Felt.....	0.000087
Paper.....	0.00040
Cotton.....	0.000040
Wool.....	0.000035
Slate.....	0.00081
Lava.....	0.00008
Pumice.....	0.00060
Cork.....	0.00072
Pine wood.....	0.00047
Oak wood.....	0.00060
Rubber.....	0.00047

A study of the above table will in many cases show the metallurgist how conduction of heat can be checked, and to what degree. The substance chosen must be able to stand the temperature without being destroyed; but it is in many cases possible to use one kind of material inside, where the heat is greatest, and a material of much poorer conductivity outside, where the heat will not destroy it. Such compound linings or coverings may be very advantageous. Infusorial earth is one of the very best insulators for moderate temperature; above

a bright red it loses efficiency greatly, and is then hardly better than powdered fire-brick.

RADIATION.

A body placed in a vacuum, with no ponderable substance in contact with it, radiates heat to its surroundings. As far as experiments have gone they show the reliability of Stefan's law, that the amount of energy radiated is proportional to the difference between the fourth powers of the absolute temperature ($C^{\circ} + 273$) of the hot body and of its surroundings. With the surroundings at 0° and the hot body at 100° , Pecelet determined the following amounts of radiation which we give here in C. S.-gram calorie units, that is, the number of gram calories radiated per square centimeter of surface, per 0° to 100° difference of temperature, with the understanding that this quantity gives the heat radiated in the range 100° and 0° . For other ranges of temperature Stefan's law would have to be used, starting with these figures as a basis; that is, the quantity of heat radiated from 100° to 0° represents a difference of 13.8×10^9 between the fourth powers of the absolute temperatures 273 and 373, and for any other numerical difference between the fourth powers of the two absolute temperatures concerned, a corresponding value for the heat radiated in that range could be calculated.

Polished silver.....	0.00054
Silvered paper.....	0.00177
Polished brass.....	0.00108
Copper.....	0.00068
Zinc.....	0.00102
Tin.....	0.00090
Polished sheet iron.....	0.00189
Leaded sheet iron.....	0.00273
Ordinary sheet iron.....	0.01164
Russian sheet iron.....	0.01410
New cast iron.....	0.01332
Oxidized cast iron.....	0.01410
Glass.....	0.01222
Paper.....	0.01583
Lamp-black.....	0.01684

Building stone.....	0.01500
Plaster.....	0.01500
Wood.....	0.01500

In order to save calculation we may deduce from Peclet's experiments that the heat radiated for other ranges of radiating temperatures is relatively (calling the above figures unity):

100° to 0° (surroundings).....	1.0
150° "	2.0
200° "	3.3
300° "	7.0
400° "	12.0
500° "	18.3
600° "	26.0
700° "	35.0
800° "	45.3
900° "	57.0
1000° "	70.0

It is thus possible to calculate the heat radiated from a hot surface, and to add it to the heat transferred to the air by contact. In practice the total heat loss from the outside surface equals the total heat coming through the walls, which at the outer surface splits into two parts. The one is transferred to air by contact, calculated from the laws of transfer already discussed, and the other radiated freely without contact, and calculated from the data just given. If the temperature of the outer solid surface is carefully taken, both of these amounts of heat can be calculated, and the sum is the total heat being lost by transmission through the wall of the furnace.

APPENDIX TO PART I.

Problem 25.

(1) Write the equations showing the relative weights and relative volumes (of gases) concerned in the combustion of

Methane (marsh gas).....	C H ⁴
Acetylene.....	C ² H ²
Ethylene (olefiant gas).....	C ² H ⁴
Methylene.....	C ² H ⁶
Allylene.....	C ³ H ⁴
Propylene.....	C ³ H ⁶
Propylene hydride.....	C ³ H ⁸
Benzine.....	C ⁶ H ⁶
Turpentine (liquid).....	C ¹⁰ H ¹⁶
Napthaline (liquid)	C ¹⁰ H ⁸

(2) The molecular heats of combustion of the above gases to CO² and liquid H²O are given by Berthelot as:

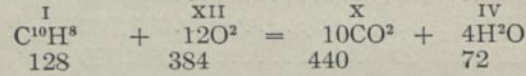
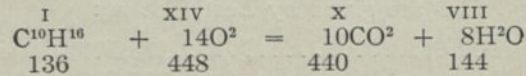
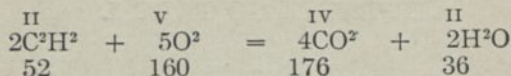
for C H ⁴	213,500	Calories
“ C ² H ²	315,700	“
“ C ² H ⁴	341,100	“
“ C ² H ⁶	372,300	“
“ C ³ H ⁴	473,600	“
“ C ³ H ⁶	499,300	“
“ C ³ H ⁸	528,400	“
“ C ⁶ H ⁶	784,100	“
“ C ¹⁰ H ¹⁶ (liquid).....	1,490,800	“
“ C ¹⁰ H ⁸ (liquid).....	1,241,800	“

(a) Calculate the molecular heats of combustion to CO² and H²O vapor.

(b) Calculate the molecular heats of formation of the hydrocarbons themselves, using (C, O²) 97,200 and (H²O) 69,000 liquid or 58,060 gas.

(c) Calculate the heat of combustion, to CO² and H²O vapor, of one cubic meter of each gas, and of one cubic foot in B. T. units.

Answers (1):



(2)

	Molecular Heat of Formation (C Amorphous.)	Molecular Heat of Combustion (to H ² O Vapor.)	Heat of Combustion of 1 m ³ (Cal.)		1 ft. ³ B. T. U.
C H ⁴	+ 21,700	+ 191,620	+ 8,623	+ 970	
C ² H ²	- 52,300	+ 304,760	+ 13,714	+ 1,543	
C ² H ⁴	- 8,700	+ 319,220	+ 14,365	+ 1,616	
C ² H ⁶	+ 29,100	+ 339,480	+ 15,277	+ 1,719	
C ³ H ⁴	- 44,000	+ 451,720	+ 20,327	+ 2,287	
C ³ H ⁶	- 700	+ 466,480	+ 20,992	+ 2,362	
C ³ H ⁸	+ 39,200	+ 486,640	+ 21,899	+ 2,464	
C ⁶ H ⁶	+ 6,100	+ 751,280	+ 33,808	+ 3,803	
C ¹⁰ H ¹⁶ (liquid)	+ 33,200	+ 1,403,280	
C ¹⁰ H ¹⁶ (gas)	+ 23,800	+ 1,412,680	+ 63,570	+ 7,152	
C ¹⁰ H ⁸ (liquid)	+ 6,200	+ 1,198,040	

Problem 26.

The following typical analyses are from Poole's book on "The Calorific Power of Fuels":

	<i>Bituminous Coal.</i> <i>"Carnegie, Pa."</i>	<i>Fuel Oil.</i> <i>"Lima, O."</i>	<i>Natural Gas.</i> <i>"Findlay, O."</i>
Carbon	77.20	80.2	H ² 1.64
Hydrogen	5.10	17.1	CH ⁴ 93.35
Oxygen	7.22	1.3	C ² H ⁴ 0.35
Nitrogen	1.68	1.4	CO ² 10.25
Sulphur	1.42		CO 0.41
Moisture	1.45		O ² 0.39
Ash	5.93		N ² 3.41
			H ² S 0.20

Required: (1) The practical, metallurgical calorific powers of

- (a) The coal, for kilogram or pound 7,447
 (b) The oil, per kilogram or pound 11,393
 (c) The gas, per cubic meter 8,143 kg. Cal.
 (d) The gas, per 1000 cubic feet 509,000 lb. Cal.

(2) Compare the calorific values of 1 ton (2240 lbs.) of coal, 1 ton (2000 lbs.) of oil, and 1000 cubic feet of natural gas.

32.8:44.8:1.

Problem 27.

The composition of some commercial gases used as fuels is given by Wyer (Treatise on Producer-Gas and Gas Producers, p. 50), as in following table:

	H ²	CH ⁴	C ² H ⁴	N ²	CO	O ²	CO ²
Natural gas (Pitts- burg).....	3.0	92.0	3.0	2.0			
Oil gas.....	32.0	48.0	16.5	3.0		0.5	
Coal gas, from re- torts.....	46.0	40.0	5.0	2.0	6.0	0.5	0.5
Coke-oven gas.....	50.0	36.0	4.0	2.0	6.0	0.5	1.5
Carburetted water- gas.....	40.0	25.0	8.5	4.0	19.0	0.5	3.0
Water gas.....	48.0	2.0		5.5	38.0	0.5	6.0
Producer gas (hard coal, using steam)	20.0			49.5	25.0	0.5	5.0
Producer gas (soft coal).....	10.0	3.0	0.5	58.0	23.0	0.5	5.0

Requirements: For each of the above gases calculate

- (1) The volume of air theoretically necessary to burn it.
- (2) The volume of the products of combustion.
- (3) The calorific power
 - (a) per cubic meter, in kilogram Calories.
 - (b) per cubic foot, in pound Calories.
 - (c) per cubic foot, in British Thermal Units.
- (4) The theoretical temperature, if burned cold with cold air (calorific intensity).

<i>Results:</i>	<i>Volume of air to burn 1 volume.</i>	<i>Volume of products per 1 volume</i>	<i>Calorific Kg. Cal. per m³.</i>	<i>Power. Lb. Cal. per ft³.</i>	<i>B.T.U. per ft³.</i>	<i>Calorific Intensity.</i>
Natural gas (Pittsburg)	9.35	10.33	8423	526	948	1852°
Oil gas.....	7.74	8.58	7350	460	828	1915°
Coal gas, from retorts..	5.79	6.50	5550	347	625	1896°
Coke-oven gas.....	5.36	6.08	5159	322	579	1892°
Carburetted water-gas..	5.06	5.77	5008	313	563	1914°
Water gas.....	2.24	2.81	2590	162	292	1928°
Producer gas (with steam).....	1.06	1.73	1290	81	146	1676°
Producer gas (ordinary)	1.13	1.98	1300	82	148	1555°

Problem 28.

An anthracite coal containing on analysis

Carbon.....	89 per cent
Hydrogen.....	3 " "
Oxygen.....	1 " "
Ash.....	7 " "

is burned under a boiler, and the ashes produced weigh, dry, 10 per cent. of the weight of the coal used. The chimney gases, dried and then analyzed, contain CO² 15.3 per cent., O² 3.5 per cent., N² 81.2 per cent., and 25.9 grams of water is obtained for each cubic meter of dry gas collected.

- Required:*
- (1) The volume of chimney gas (measured dry) produced per kilo. of coal burned 10.41 m³.
 - (2) The volume of air used, measured dry at normal conditions, per kilo. of coal burned 10.67 m³.
 - (3) The weight of dry air used 13.80 kg.
 - (4) The volume of dry air theoretically necessary for the complete combustion of one kilo. of coal 8.72 m³.

- (5) The excess of air used, in percentage of that theoretically necessary for the perfect combustion of the coal 22.36%
- (6) The volume of chimney gas, at standard conditions, per kilo. of coal burned 10.74 m³.

Problem 29.

An anthracite coal contains

Carbon.....	89 per cent.
Hydrogen.....	3 "
Oxygen.....	1 "
Ash.....	7 "

It is burned on a grate, using 15 per cent. more air than is theoretically needed for its perfect combustion. The ashes weigh 10 kilos. per 100 kilos. of coal burned.

Required: (1) The volume of air (assumed dry and at standard conditions) used per kilo. of coal burned 9.71m³.

(2) The number of cubic feet of air per pound of coal 155.4.

(3) The percentage composition (by volume, of course) of the chimney gas, assuming it contains no soot or unburned gas. N² 77.9, CO² 16.1, O² 2.6, H²O 3.4.

(4) The percentage composition of the same, if first dried and then analyzed N² 80.6, CO² 16.7, O² 2.7.

(5) The number of grams of moisture carried per cubic meter of dried gas measured 28.4.

(6) The number of grains per cubic foot 12.4.

(7) The volume of the chimney gases, at standard conditions, (water assumed uncondensed) per kilo. of coal burned 9.85 m³.

(8) The number of cubic feet of products per pound of coal 157.6.

(9) The volume of the products in cubic meters at 350° C. and 700 m.m. pressure 24.4.

(10) The volume of the products in cubic feet at 600° F. and 29 inches pressure 349.6

Problem 30.

A bituminous coal contains

Carbon.....	75 per cent.
Hydrogen.....	5 "
Oxygen.....	10 "
Ash.....	10 "

It is powdered and injected into a cement kiln with 25 per cent. more air than is theoretically necessary for its complete combustion. The kiln calcines 200 barrels of cement daily, using 125 pounds of coal per barrel of cement. Assume outside air at 0° C. Hot gases enter stack at 819° C. Omit from calculation the water vapor and carbonic acid gas expelled from the charge.

Required: (1) The volume of air per minute which the blower or fan must furnish. 2,672 ft³.

(2) The volume of the hot products of combustion per minute, as they pass into the stack. 11,044 ft³.

Problem 31.

A bituminous coal (as of Problem 27) contains

Carbon.....	75	per cent.
Hydrogen.....	5	"
Oxygen.....	10	"
Ash.....	10	"

It is burned under a boiler with 25 per cent. more air than is theoretically necessary for its complete combustion. Assume combustion perfect, and no unburnt carbon to remain in the ashes. The wet steam produced contains 3 per cent. of water of priming, and 8.82 pounds of water is evaporated per pound of coal burnt. Steam pressure 6 atmospheres effective pressure. Outside air 0° C., feed water 10° C., stack gases 310° C.

Required: (1) The calorific power of the coal, by calculation, water formed considered uncondensed, in pound calories per pound of coal, and British Thermal Units per pound. 7096; 12773.

(2) The percentage of the calorific power of the coal represented by the heat in the dry steam produced 78.0.

(3) ditto in the water of priming 0.6.

(4) ditto in the sensible heat of the chimney gases 14.5.

(5) ditto lost by radiation and conduction 6.9.

(6) What increase in the net efficiency (requirement 2) would be obtained by using a feed water heater, which abstracted 60 per cent. of the sensible heat in the chimney gases, all other conditions remaining constant? 8.6%.

Problem 32.

A bituminous coal contains (as in Problems 27 and 28):

Carbon.....	75	per cent.
Hydrogen.....	5	“
Oxygen.....	10	“
Ash.....	10	“

It is blown into a revolving cylindrical furnace with a high pressure blast which supplies only 14.9 per cent. of the air necessary for its complete combustion, producing near the burner a highly luminous flame surrounded by a cylindrical sheath of auxiliary air drawn in by the injector action of the fuel-air jet. Assuming that in the body of the jet the hydrogen only of the coal is consumed, the luminosity being due to unconsumed particles of carbon, and ash; that the mean specific heat of carbon is $0.5 - \frac{120}{t}$, of the ash 0.25

Required: (1) The theoretical temperature of the interior of the jet of burning fuel 1140°C.

(2) The temperature if the supply of air in the fuel jet is increased to that theoretically necessary for perfect combustion of the whole fuel 1671°C.

Problem 33.

Calculate the maximum temperature obtainable in the region of the tuyers of a blast-furnace.

- (1) Using cold, dry air.....1683° C.
- (2) Using dry air, heated to 700° C. 2272° C.
- (3) Using moist air, heated to 700° C., the amount of moisture present being such as air at 37° C. can carry when saturated with moisture. 1947° C.
- (4) Using cold, moist air of above composition. 1367° C.

Problem 34.

Powdered coal having the following composition is burnt in a cement kiln:

Carbon.....	73.60	per cent.
Hydrogen.....	5.30	“
Nitrogen.....	1.70	“
Sulphur.....	0.75	“

Oxygen.....	10.00	per cent.
Ash.....	8.05	“
Moisture.....	0.60	“

The finely-ground coal is burnt by cold air, at 20° C., and 760 m.m. pressure. The gases resulting, together with carbon dioxide gas from the charge, pass into the stack at 820° C. The analysis of the flue gases, by volume, dried before analysis, is:

Carbon dioxide.....	25.9	per cent.
Oxygen.....	3.1	“
Carbon monoxide.....	0.2	“
Sulphur dioxide.....	not determined.	
Nitrogen.....	difference.	

Of the carbon dioxide in the gases assume 40 per cent. of it to come from the carbonates in the charge being treated, and not from the coal. Assume no water in the furnace charge. The air used is saturated with moisture, at 20° C., tension of the moisture 22 m.m. of mercury.

- Required:* (1) The theoretical calorific power of the coal 7525.
 (2) The theoretical temperature of the hottest part of the flame 1593° C.
 (3) The proportion of the calorific power of the fuel carried out by the hot gases 50.4%.
 (4) The percentage excess of air admitted above that theoretically required 16.4%.

Problem 35.

Calculate the draft of a chimney, in inches of water gauge and feet of cold air, if measured at its base, its height being 120 feet, inside diameter, (round) 6 feet, temperature of gases inside at bottom 300° C., at top 200° C., specific gravity (air = 1) 1.03, and taking in 200 cubic feet (measured at 0° and 760 m.m.) of products of combustion per second. Section inside uniform top to bottom, sides fairly smooth, assume $K = 0.04$. Outside temperature 0° C. 0.91 in.; 59.25 ft.

Problem 36.

A copper cylinder weighing 22.092 grams was placed in a small iron box on the end of a rod, and held several minutes in the hot blast main of a blast-furnace. On removal, and drop-

ping instantly into a calorimeter, containing 301.3 grams of water, the temperature rose $4^{\circ}.183$ C. in three minutes. From previous experiments with this calorimeter, it was known that in three minutes it would abstract from the water 30 gram calories for each 1° observed rise of temperature above starting. The mean specific heat of copper between 0° and t° being $0.09393 + 0.00001778t$, what was the temperature of the hot-blast?

[N.B.—Calculate what would theoretically have been the temperature of the water of the calorimeter if no heat had been lost to the calorimeter, and work out using this as the final temperature of the water.] 618° C.

Problem 37.

A piece of tin-stone (Cassiterite, SnO_2) from Bolivia was tested to obtain its specific heat. It was heated to two temperatures determined by a Le Chatelier thermo-electric pyrometer, and dropped into a calorimeter. Corrections for calorimeter losses were made as explained in the *Journal of the Franklin Institute*, August, 1901. Data of the two tests were as follows:

	<i>Experiment 1.</i>	<i>Experiment 2.</i>
Weight of tin-stone used.....	12.765 gms.	12.765 gms.
Temperature of same.....	476° C.	1018° C.
Weight of water in calorimeter...	299.4 gms.	300.7 gms.
Temperature of same, starting....	$16^{\circ}.527$	$18^{\circ}.705$
Temperature of same, 3 minutes..	$18^{\circ}.444$	$22^{\circ}.985$
Water value of calorimeter per 3', for each 1° rise.....	30 cal.	30 cal.
<i>Required:</i> A formula of the form $S_m = \alpha + \beta t$, for the particular piece of Cassiterite used.	$0.1050 + 0.0000061t$	

Problem 38.

The chimney gases from a boiler enter the stack at a temperature of 400° C. Their composition is:

Carbon dioxide.....	15.0 per cent.
Oxygen.....	5.9 “
Nitrogen.....	79.1 “

What percentage of the total calorific power of the coke burnt will be saved by using a feed-water heater which reduces the

temperature of these gases to 200° C. and sends 75 per cent. of the heat thus abstracted into the boiler with the feed-water? 7.92%.

Problem 39.

A blast-furnace gas contains, by volume:

Carbon monoxide.....	23	per cent.
Carbon dioxide.....	12	"
Hydrogen.....	2	"
Methane.....	2	"
Water vapor.....	3	"
Nitrogen.....	58	"

Its temperature is 20° C., and it is taken to a gas engine, mixed with the theoretical amount of dry air needed for perfect combustion, and compressed to 4 atmospheres tension (total pressure) before being ignited. Neglect the heating of the gas-air mixture by compression, *i.e.*, assume the temperature of the compressed mixture 20° C. before ignited. Assume that at the instant of ignition the volume occupied by the gases remains constant, so that the specific heat at constant volume applies. (Specific heat of 1 cubic meter at constant volume equals specific heat at constant pressure—0.09.)

Required: (1) The calorific power of the gas per cubic meter, at constant pressure, and at constant volume. 928.5; 925.5.

(2) The theoretical temperature at the moment after ignition has taken place. 1592° C.

(3) The maximum pressure exerted. $22\frac{2}{3}$ atmospheres.

(4) The volume of gas needed per horse-power hour, at a mechanico-thermal efficiency of 30 per cent. 2.81 m³, at 20° C.

Problem 40.

Bituminous coal containing carbon 78 per cent., hydrogen 5, oxygen 8, ash 8, water 1, is used in a gas producer. Assume the calorific power of the coal (water formed uncondensed) as 7480 Calories; ashes formed 12 per cent. Gas formed leaves producer at 600° C.; composition:

Carbon monoxide.....	35	per cent.
Carbon dioxide.....	5	"
Methane.....	5	"
Hydrogen.....	5	"
Nitrogen.....	50	"

Required: (1) The volume of gas obtained per kilo. of coal burnt. 3.045 m³

(2) The calorific power of the gas per cubic meter. 1633 Calories.

(3) The proportion of the calorific power of the fuel obtainable on burning the gas. 66.5 per cent.

(4) The proportion of the calorific power of the fuel which has been sacrificed in making the gas, assuming it burnt cold. 33.5 per cent.

Problem 41.

Producer gas of the following composition:

Carbon monoxide.....	28	per cent.
Carbon dioxide.....	4	"
Hydrogen.....	4	"
Methane.....	2	"
Water vapor.....	1	"
Nitrogen.....	61	"

is burned with 10 per cent. more air than theoretically required, both air and gas being preheated to 1000° C.

Required: The theoretical maximum temperature of the flame. 1600° C.

Problem 42.

Kiln-dried peat from Livonia contained by analysis:

Carbon.....	49.70	per cent.
Hydrogen.....	5.33	"
Oxygen.....	30.76	"
Nitrogen.....	1.01	"
Ash.....	13.23	"

The wet peat, as taken from the ground, carried 75 per cent. of water, when air-dried 20 per cent., and when kiln-dried none, as per analysis.

The air-dried peat is dried in a kiln by means of a current of hot air, which enters the kiln, and comes in contact with the freshly-charged peat, at a temperature of 150° C., while it leaves the kiln, near the discharge end, at 50° C. Outside temperature 0° C., outside air dry. The kiln loses by radiation 10 per cent. of the sensible heat of the hot air coming into it, the rest represents the sensible heat of the warm moist air and

dried peat, issuing at 50°C ., and the heat necessary to evaporate the moisture. The air required is heated in a stove where kiln-dried peat is burned, 75 per cent. of the heat generated being transferred to the air. Mean specific heat of kiln-dried peat 0.25.

Required: (1) The practical calorific powers of wet peat, air dried peat and kiln dried peat. 607; 3278; 4249.

(2) The volume of air, at standard conditions, needed for drying one metric ton of air-dried peat. $5,122\text{ m}^3$

(3) The percentage degree of saturation, with moisture, of the issuing air. 35.4

(4) The amount of kiln-dried peat required to be burned in the stove per ton of air-dried peat put through the kiln, and the percentage of the total fuel necessary for this purpose.

70.5 kg · 9.25%

Problem 43.

A set of four coke ovens produce 10,000 cubic feet of gas per hour, measured at 60°F ., and having the composition H^2 64.3 per cent., CO 20.7, CH^4 5.4, C^2H^4 0.5, C^6H^6 0.5, CO^2 2.0, O^2 1.0, N^2 5.6 per cent. Temperature leaving the ovens 2900°F . For half of each hour the whole gas is burned by the theoretical amount of cold air, as it passes into recuperators, whence the products at 1900°F . pass under steam boilers where their temperature is reduced to 500° before passing to the stack. For the second half of each hour the gases pass through the recuperators unmixed with air, are there heated to 1900°F ., and at that temperature pass under boilers where they meet with the theoretical quantity of air needed for combustion, are burned, and the products pass to the stack at 500°F .

Required: (1) The horse-power of the boilers during the first 30 minutes, calling 1 horse-power the ability to evaporate $34\frac{1}{2}$ pounds of water per hour at 212°F ., and assuming the boilers to produce steam representing 50 per cent. of all the heat received by them and generated within them (net efficiency 50 per cent.). 23.4 H. P.

(2) The same, for the second 30 minutes. 57.0 H. P.

Problem 44.

A plant of by-product coke ovens uses bituminous coal containing 76 per cent. of carbon, and having a calorific power

of 9000, produces coke containing an average of 86 per cent. of carbon, and having a calorific power of 7000, while the by-product tar produced contains 20 per cent. of carbon. The coke weighs 70 per cent. and the tar 5 per cent. of the weight of the coal used. The average analysis of the gases for the month of January, 1904 (samples dried before analysis) was:

Carbon dioxide.....	3.00	per cent.
Oxygen.....	0.50	"
Carbon monoxide.....	5.10	"
Marsh gas, CH ⁴	35.00	"
Illuminants { C ² H ⁴	2.13	"
{ C ³ H ⁸	1.06	"
{ C ⁶ H ⁶	1.06	"
Hydrogen.....	40.00	"
Nitrogen.....	12.15	"

Required: (1) The volume of by-product gases, at standard barometric pressure and at 60° F., produced per ton (2000 pounds) of coal used. 16,294 cubic feet.

(2) The proportion of the calorific power of the coal represented by the calorific powers of the coke and the gases. 54.4%; 27.4%.

(3) Using half the gases produced in gas-engines, at an efficiency of conversion into power of 25 per cent., how many horse-power-hours could be thus generated per pound of coal coked? 0.22 H. P. hours.

Problem 45.

A gas producer uses coal which analyzed: total carbon 75.68 per cent., oxygen 12.70 per cent., hydrogen 4.50 per cent., ash 7.12 per cent. The ashes produced contain 21.07 per cent. of unburnt carbon. The gas carried 30.4 grams of moisture to each cubic meter of dried gas collected, and the latter shows on analysis:

Carbon dioxide.....	5.7	per cent.
Carbon monoxide.....	22.0	"
Methane (CH ⁴).....	2.6	"
Ethylene (C ² H ⁴).....	0.6	"
Hydrogen.....	10.5	"
Oxygen.....	0.4	"
Nitrogen.....	58.2	"

A steam blower furnishes blast, forcing in the outside air which carries 15 grams of moisture per cubic meter, measured dry at 20° C.

Required: (1) The volume of gas (dry) produced per kilo. of coal used. 4.337 m³.

(2) The weight of steam used by the blower per kilo. of coal used. 0.2691 kg.

(3) The weight and volume of air blown in, per kilo. of steam used by the blower. 15.5 kg.; 12.95 m³.

(4) The percentage of the steam blown in which is not decomposed in the producer, assuming the moisture in the gas to represent steam used and not decomposed (assumption not strictly accurate). 49.3%.

(5) The mechanical efficiency of the blower, assuming it uses steam at 4 atmospheres effective pressure, and produces 10 centimeters of water gauge pressure in the ash pit of the producer. 4.67%.

Problem 46.

Assume the gas of Problem 42 to be produced by the combustion of 1000 kilos. of coal per hour in the producers, and to be burned in a furnace with such excess of air (carrying at 20° C. 15 grams of moisture per cubic meter measured dry) that the chimney gas, analyzed dry, contains:

Carbon dioxide.....	12.7 per cent.
Nitrogen.....	80.6 "
Oxygen.....	6.7 "

These products of combustion enter the chimney at 500° C. and leave it at 350° C., their velocity entering at the base is 4 meters per second. Outside air 20°. The efficient draft is 2.5 centimeters of water gauge, measured at the base; assume this 90 per cent. of the total head of the chimney.

Required: (1) The diameter of the chimney, assuming it round, and its height, assuming its section uniform.

1.52 meters; 41.3 meters.

(2) The work done by the chimney, expressed in horse-power. 2.6

(3) The energy efficiency of the chimney, *i.e.*, the ratio of the mechanical work it performs to the mechanical equivalent of the heat which it receives. 0.079 per cent.

Problem 47.

Assume the chimney of Problem 46 to be built of fire-brick of an average thickness of 60 centimeters; that the gases passing through per hour are 1586 cubic meters of nitrogen and air, 315 cubic meters of carbon dioxide and 234 cubic meters of water vapor; the temperature at the base is 500° C., at the top 350°; the velocity of the hot gases at the base, 4 meters per second; diameter 1.52 meters, height 41.3 meters. Assume further the coefficient of transfer of heat from gas to brick and brick to air to be $\frac{2+100\sqrt{v}}{36,000}$ (in C. G. S. units), and the velocity of the wind outside to be 20 kilometers per hour.

Required: The coefficient of conductivity of the fire-brick in C. G. S. units. 0.31

HEAT CONTENT OF PURE IRON.

P. Oberhoffer has conducted very exact determinations of the heat content of iron up to 1500° (*Metallurgie* June 22, July 8 and 22, 1907), and J. W. Richards has extended the figures, by assumptions, up to 2000° C. (*Electrochemical and Metallurgical Industry*, Sept. 1907, p. 366). The results arrived at, for Q at temperature t, reckoning from 0° C, are as follows:

t	Q	t	Q
250	30.5	1200	200.0
300	37.7	1250	208.3
350	45.0	1300	216.1
400	52.2	1350	224.2
450	60.3	1400	233.1
500	68.3	1450	241.4
550	76.7	1500	250.0
600	85.0	1550	258.3
650	95.1	1600	266.7
700	111.8	1600	336.0
750	125.6	1650	346.0
800	135.8	1700	356.0
850	144.4	1750	366.0
900	152.8	1800	376.0
950	160.4	1850	386.0

320
328

t	Q	t	Q
1000	167.8	1900	396.0
1050	175.4	1950	406.0
1100	183.0	2000	416.0
1150	191.7		

A study of these figures shows an absorption of about 10 Cal. rendered latent, between 650° and 700°, a probable absorption of 2 Cal. about 850°. Specific heat above 900 almost constant, —0.167. Sm (t to o), when it is between 1000 and 1500—0.167. Assumed specific heat liquid, 0.20.

HEATS OF FORMATION

OXIDES.

(See page 16 for these tables expressed in different form)

	ANHYDROUS.			TO DILUTE SOLUTION.		
	Per unit of Base	Per unit of Oxygen	Per unit of Compound	Per unit of Base	Per unit of Oxygen	Per unit of Compound
Mg O	5,975	8,963	3,585	6,200	9,300	3,720
Ba O	974	8,338	872	1,179	10,938	1,051
Ca O	3,288	8,219	2,348	3,740	9,350	2,671
Sr O	1,508	8,200	1,274	1,821	9,900	1,538
Al ² O ³	7,270	8,179	3,849
Na ² O	2,193	6,306	1,627	3,389	9,744	2,515
K ² O	1,259	6,138	1,045	2,118	10,325	1,758
Si O ²
Mn O	1,653	5,681	1,280
B ² O ³	12,391	5,679	3,894	12,723	5,831	3,999
Zn O	1,305	5,300	1,058
Mn ³ O ⁴	1,988	5,125	1,434
P ² O ⁵	5,895	4,566	2,572
Ba O ²	1,062	4,542	861
Sn O	599	4,419	527
Cn O ²	1,197	4,416	942
C O ² (from CO, O)	2,430	4,253	1,546	2,641	4,621	1,680
H ² O
Product solid	35,200	4,400	3,911
Product liquid	34,500	4,313	3,833
Product gas	29,030	3,629	3,226
Fe ³ O ⁴	1,612	4,231	1,167
Cd O	592	4,144	518
Fe O	1,173	4,106	913
Fe ² O ³	1,746	4,075	1,223
Co O	1,086	4,006	855
Mn O ²	2,278	3,916	1,440
Ni O	1,051	3,844	826
Sb ² O ³	695	3,479	580
As ² O ³	1,043	3,258	790	993	3,102	752
Pb O	245	3,175	228
C O ² (from C)	8,100	3,038	2,209	8,592	3,222	2,343
Bi ² O ³	335	2,900	300
Sb ² O ⁵	963	2,890	723
As ² O ⁵	1,463	2,743	954	1,503	2,818	980
Cu ² O	344	2,738	306
Tl ² O	105	2,675	101	97	2,481	94
Cu O	593	2,356	474
S O ² (gas)	2,164	2,164	1,082	2,425	2,425	1,213
Pb O ²	306	1,981	265

	ANHYDROUS.			TO DILUTE SOLUTION.		
	Per unit of Base	Per unit of Oxygen	Per unit of Compound	Per unit of Base	Per unit of Oxygen	Per unit of Compound
S O ³	2,872	1,915	1,149	4,406	2,938	1,763
Tl ² O ³	215	1,825	192
C O (gas)	2,430	1,823	1,041
S O ³						
(from S O ² &O)	354	1,415	283	991	3,963	793
Hg ² O	56	1,388	53
Hg O	108	1,344	100
Te O ²	624	2,447	497
Pd O	198	1,313	172
Pt O	87	1,063	81
Pb O ²						
(from PbO&O)	56	788	53
Ba O ²						
(from BaO&O)	79	756	72
Ag ² O	32	438	30
Au ² O ³	-29	-240	-26

HYDRATES.

From Metallic Oxide and Water.

	ANHYDROUS.			TO DILUTE SOLUTION.		
	Per unit of Oxide	Per unit of Water	Per unit of Hydrate	Per unit of Oxide	Per unit of Water	Per unit of Hydrate
Mg O. H ² O	135	300	93
Sr O. H ² O	166	950	141	264	1,511	225
Ca O. H ² O	270	839	204	323	1,006	245
K ² O. H ² O	447	2,333	375	713	3,722	598
Na ² O. H ² O	573	1,972	444	887	3,056	688
Al ² O ³ . 3H ² O	29	56	19
S O ³ . H ² O	391	1,739	319	616	2,739	503
N ² O ⁵ . H ² O	9	56	8
Tl ² O. H ² O	7	167	7
Bi ² O ³ . 3H ² O	-6	-52	-5

SULPHIDES.

	ANHYDROUS.			TO DILUTE SOLUTION.		
	Per unit of Base	Per unit of Sulphur	Per unit of Sulphide	Per unit of Base	Per unit of Sulphur	Per unit of Sulphide
Li ² S	8,244	3,606	2,509
K ² S	1,327	3,234	941	1,455	3,547	1,032
Ba S	751	3,216	609	801	3,431	650
Sr S	1,141	3,103	834	1,226	3,334	897
Ca S	2,358	2,947	1,310	2,515	3,144	1,397
Na ² S	2,152	2,791	1,145	2,267	3,259	1,337
Mg S	3,308	2,481	1,418
Mn S	829	1,425	524
Zn S	662	1,344	443

	ANHYDROUS.			TO DILUTE SOLUTION.		
	Per unit of Base	Per unit of Sulphur	Per unit of Sulphide	Per unit of Base	Per unit of Sulphur	Per unit of Sulphide
Al ² S ³	2,341	1,317	843
Cd S	307	1,075	239
Fe S	428	750	273
Co S	371	685	241
Tl ² S	106	675	92
Cu ² S	160	634	127
Pb S	98	631	85
Si S ²	1,429	625	435
Ni S	333	609	215
Sb ² S ³	143	358	102
Hg S	53	331	46
Cu S	159	316	106
H ² S (gas)	2,400	150	141	4,750	297	279
Ag ² S	14	94	12
C S ² (gas)	-2,117	-397	-334

FLUORIDES.

	ANHYDROUS.			TO DILUTE SOLUTION.		
	Per unit of Base	Per unit of Fluorine	Per unit of Compound	Per unit of Base	Per unit of Fluorine	Per unit of Compound
Sr F ²	2,575	5,898	1,792
Ba F ²	1,635	5,895	1,280	1,617	5,829	1,266
Li F	16,696	6,151	4,496
K F	2,821	5,789	1,897	2,913	5,979	1,959
Ca F ²	5,411	5,696	2,775
Mg F ²	8,729	5,513	3,379
Na F	4,770	5,775	2,612	4,744	5,743	2,598
N H ⁴ F	5,625	5,329	2,736	5,542	5,250	2,696
Al F ³	10,193	4,828	3,276
B F ³	19,940	3,848	3,226
Mn F ²	2,787	4,034	1,648
Zn F ²	2,127	3,637	1,342
Si F ⁴	9,854	3,631	2,653
			(gas)			
Fe F ²	2,236	3,295	1,332
Cd F ²	1,087	3,203	811
Co F ²	2,040	3,167	1,241
Ni F ²	2,034	3,131	1,233
Fe F ³	2,947	2,894	1,460
Tl F	267	2,863	244
Pb F ²	491	2,674	415
H F	38,500	2,026	1,925	50,300	2,647	2,515
			(gas)			
Sb F ³	1,139	2,398	772
Cu F ²	1,386	2,320	868
Ag F	204	1,162	174	236	1,341	201

CHLORIDES.

	ANHYDROUS.			TO DILUTE SOLUTION.		
	Per unit of Base	Per unit of Chlorine	Per unit of Compound	Per unit of Base	Per unit of Chlorine	Per unit of Compound
K Cl	2,710	2,977	1,419	2,595	2,879	1,358
Be Cl ²	17,222	2,183	1,938	22,167	2,810	2,494
Ba Cl ²	1,439	2,776	948	1,447	2,793	953
Na Cl	4,257	2,758	1,674	4,200	2,721	1,651
Li Cl	13,414	2,645	2,209	14,614	2,882	2,407
Sr Cl ²	2,123	2,601	1,169	2,251	2,758	1,240
Ca Cl ²	4,248	2,393	1,531	4,685	2,639	1,688
N H ⁴ Cl	4,267	2,192	1,209	4,044	2,051	1,146
Mg Cl ²	6,300	2,129	1,592	7,796	2,635	1,969
Al Cl ³	5,993	1,519	1,212	8,819	2,236	1,784
Mn Cl ²	2,037	1,577	889	2,327	1,803	1,016
Zn Cl ²	1,498	1,372	716	1,738	1,592	831
Tl Cl	238	1,369	203	188	1,082	1,060
Cd Cl ²	837	1,320	512	861	1,358	527
Pb Cl ²	405	1,182	302	376	1,097	280
Fe Cl ²	1,468	1,158	647	1,788	1,410	788
Sn Cl ²	686	1,139	428
Co Cl ²	1,300	1,080	590	1,610	1,338	731
Ni Cl ²	1,277	1,052	577	1,605	1,323	725
Cu Cl	557	997	358
Sn Cl ⁴	1,100	914	499
			(liquid)			
Fe Cl ³	1,717	903	592	2,283	1,200	787
Hg Cl	157	882	133
Sb Cl ³	762	858	404
Bi Cl ³	437	853	289
Si Cl ⁴	4,600	907	758
			(gas)			
B Cl ³	8,100	837	758
			(gas)			
Ag Cl	269	817	202
Hg Cl ²	267	751	197	252	708	185
Cu Cl ²	808	724	382	983	880	464
As Cl ³	953	671	394
H Cl	22,000	620	603	39,400	1,110	1,080
Sb Cl ⁵	871	589	351
			(liquid)			
Pd Cl ²	382	570	229
Pt Cl ⁴	308	424	179	409	562	237
Au Cl ³	116	214	75	138	255	90
Au Cl	29	163	25

CARBONATES.

Reaction $R O. C O^2$

	ANHYDROUS.			IN DILUTE SOLUTION.		
	Per unit of Base	Per unit of Acid	Per unit of Compound	Per unit of Base	Per unit of Acid	Per unit of Compound
Ba O. C O ²	364	1,266	282
K ² O. C O ²	922	1,970	628	216	461	147
Sr O. C O ²	515	1,205	361
Ca O. CO ²	806	1,026	451
Na ² O. CO ²	1,219	1,718	713	328	461	192
Mg O. CO ²	733	666	349
Mn O. CO ²	313	505	193
Zn O. CO ²	191	352	124
Fe O. CO ²	346	566	215
Cd O. CO ²	154	448	115
Pb O. CO ²	99	500	83
Cu O. CO ²	140	255	91
Ag ² O. CO ²	82	445	71

NITRATES.

Reaction $R O. N^2 O^5$

K ² O. N ² O ⁵	1,500	1,306	698	294	256	137
Na ² O. N ² O ⁵	1,963	1,127	716	443	255	162
Zn O. N ² O ⁵	226	169	97
Pb O. N ² O ⁵	250	517	168	84	174	57
Cu O. N ² O ⁵	188	139	80
H ² O. N ² O ⁵	56	9	8
Ag ² O. N ² O ⁵	222	478	152	45	96	31

PHOSPHATES.

Reaction $3R O. P^2 O^5$.

	ANHYDROUS.			IN DILUTE SOLUTION.		
	Per unit of Base	Per unit of Acid	Per unit of Compound	Per unit of Base	Per unit of Acid	Per unit of Compound
3Ca O. P ² O ⁵	949	1,123	514
3Mg O. P ² O ⁵	959	811	439
3Na ² O. P ² O ⁵	1,273	1,668	722

SILICATES.

Reaction $R O. Si O^2$

Ba O. Si O ²	96	245	69
Ca O. Si O ²	319	298	154
2Ca O. Si O ²	253	472	165
3Ca O. Si O ²	170	476	125
Sr O Si. O ²	174	298	110
Al ² O ³ . 2Si O ²	146	124	67
Na ² O. Si O ²	729	753	371

METALLURGICAL CALCULATIONS.

	ANHYDROUS.		IN DILUTE SOLUTION.			
	Per unit of Base	Per unit of Acid	Per unit of Compound	Per unit of Base	Per unit of Acid	Per unit of Compound
3Ca O. Al ² O ³ . 2Si O ²	288	404	124
(CaO)						
	475					
(Al ² O ³)						
2H ² O. Al ² O ³ . 2Si O ²	1,023	307	143
(H ² O)						
	361					
(Al ² O ³)						
Mn O. Si O ²	76	90	41
Fe O. Si O ²	124	148	67

ALUMINATES.

Reaction R O. Al² O³.

Ca O. Al ² O ³	8	4	3
2Ca O. Al ² O ³	29	32	15
3Ca O. Al ² O ³	12	19	7

SULPHATES.

Reaction R O. S O³.

K ² O. SO ³	1,640	1,925	886	335	394	181
Ba O. SO ³	746	1,426	490
Sr O. SO ³	1,040	1,339	585
Na ² O. SO ³	2,182	1,691	953	510	395	226
Ca O. SO ³	1,679	1,175	692	557	390	229
Mg O. SO ³	1,640	820	547	783	391	261
Al ² O ³ . 3SO ³	2,073	880	619
Mn O. SO ³	938	833	441	1,133	1,005	533
Zn O. SO ³	653	661	328	880	891	442
Fe O. SO ³	392	353	185
Co O. SO ³	317	298	153
Ni O. SO ³	352	328	170
Fe ² O ³ . 3SO ³	199	133	80
Tl ² O. SO ³	206	1,087	174	77	410	65
Cd O. SO ³	482	771	296	577	917	352
Pb O. SO ³	327	913	558
H ² O. SO ³	1,606	374	295	2,606	599	679
Cu O. SO ³	655	651	328	852	848	427
Hg ² O. SO ³	146	761	122
Ag ² O. SO ³	294	853	217	275	797	203
Hg O. SO ³	239	646	174

BORATES.

Reaction R O. B² O³.

Na ² O. (B ² O ³) ²	1,645	729	505	687	304	211
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AMALGAMS.
Reaction R. Hg.

	DILUTE AMALGAM					
	Per unit of Metal	Per unit of Mercury	Per unit of Amalgam	Per unit of Metal	Per unit of Mercury	Per unit of Compound
Hg ¹² K	14	887	14	11	656	10
Hg ⁴ K	37	762	35	32	656	31
Hg ⁶ Na	18	952	18	16	826	16
Hg ⁴ Av	13
Hg ⁴ Ag	23

ALLOYS.

(Cu Zn ²)	160	78	52
(Cu Zn)	91	89	45
(Cu ³ Al)	141	997	124
(Cu ² Al)	167	788	138
(Cu Al ²)	91	322	71
(Cu Al)	30	70	21
(Cu ² Al ³)	80	126	49
(Cu Al ²)	106	124	57

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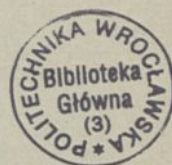
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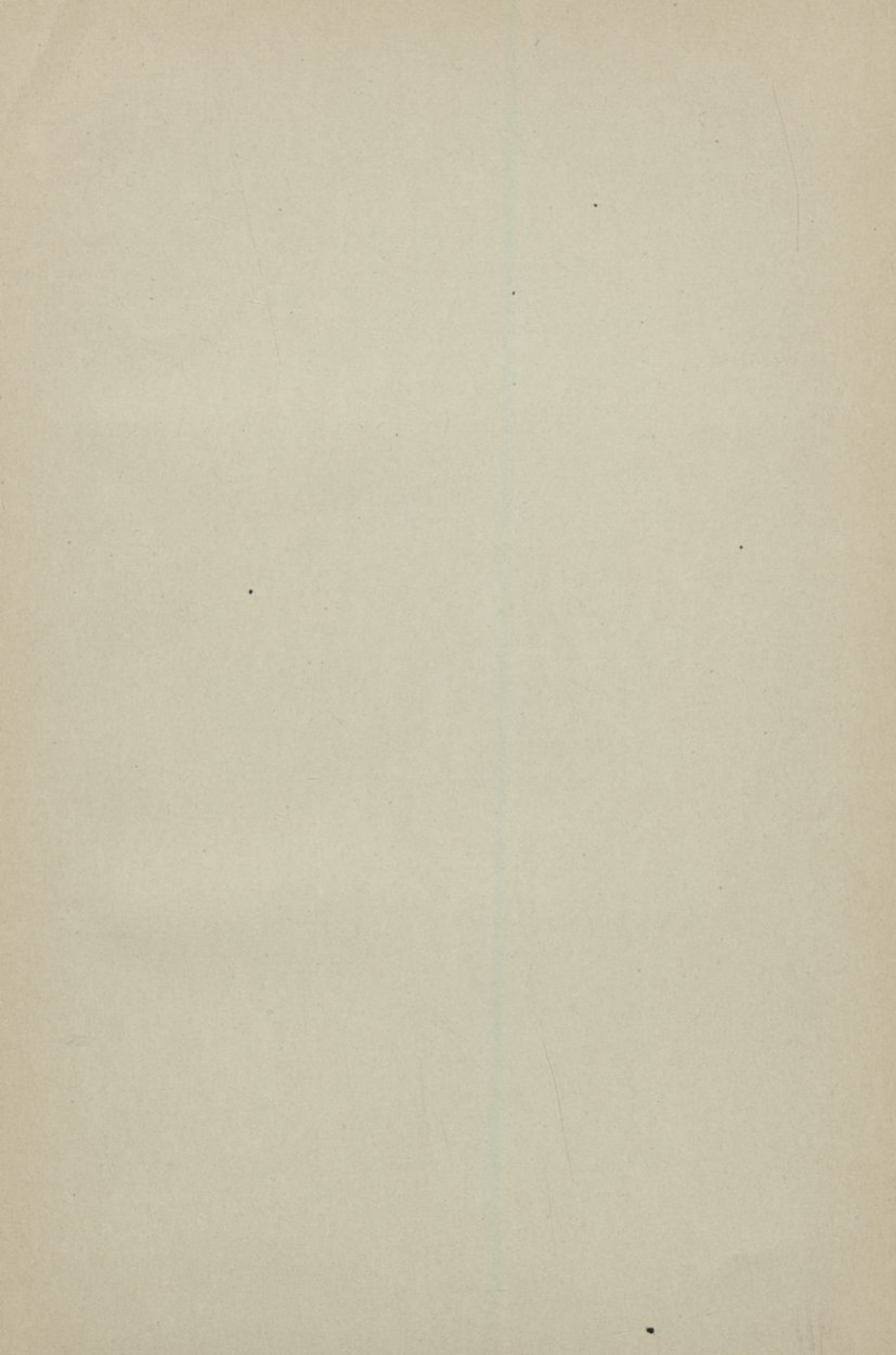
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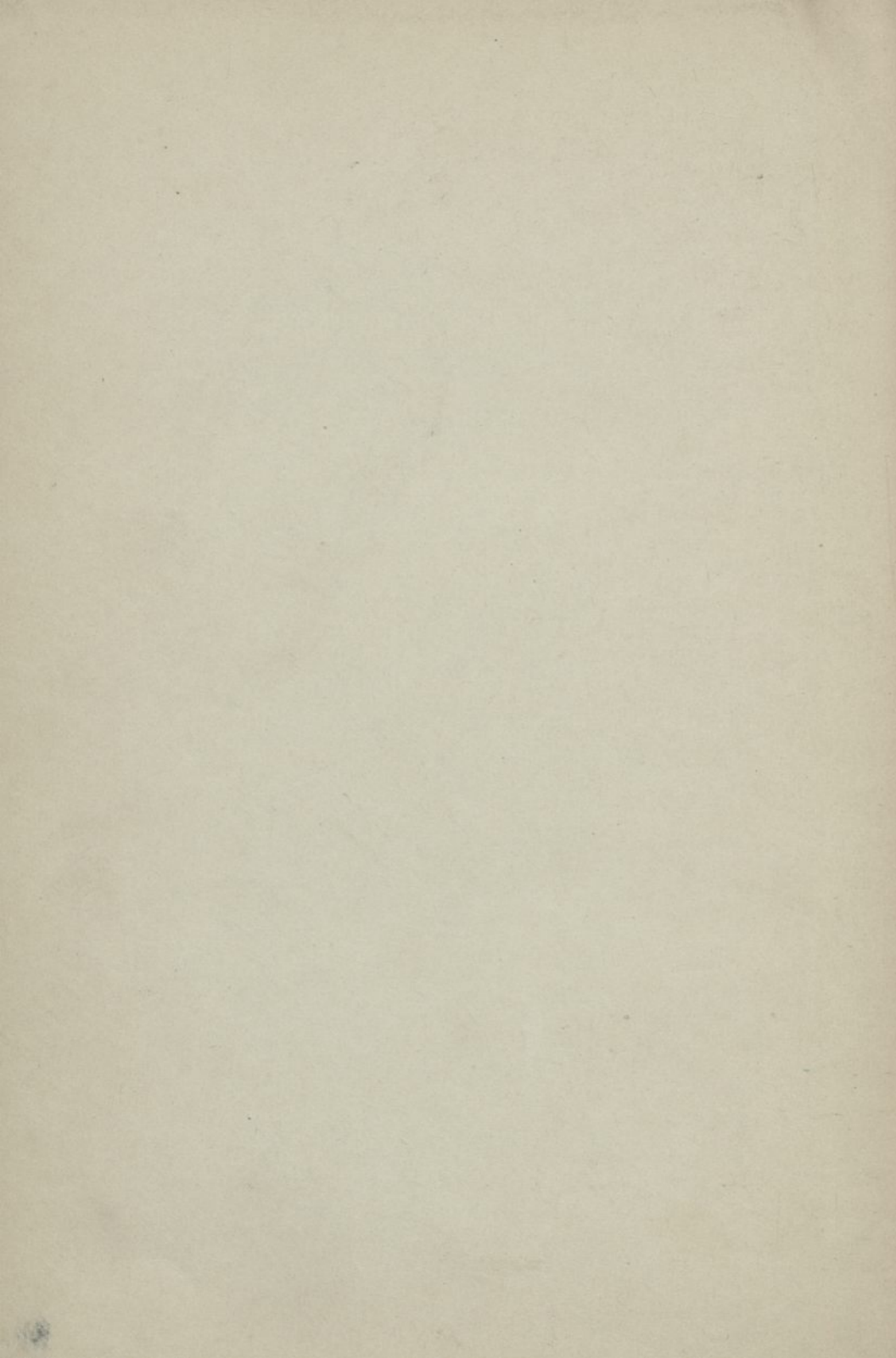
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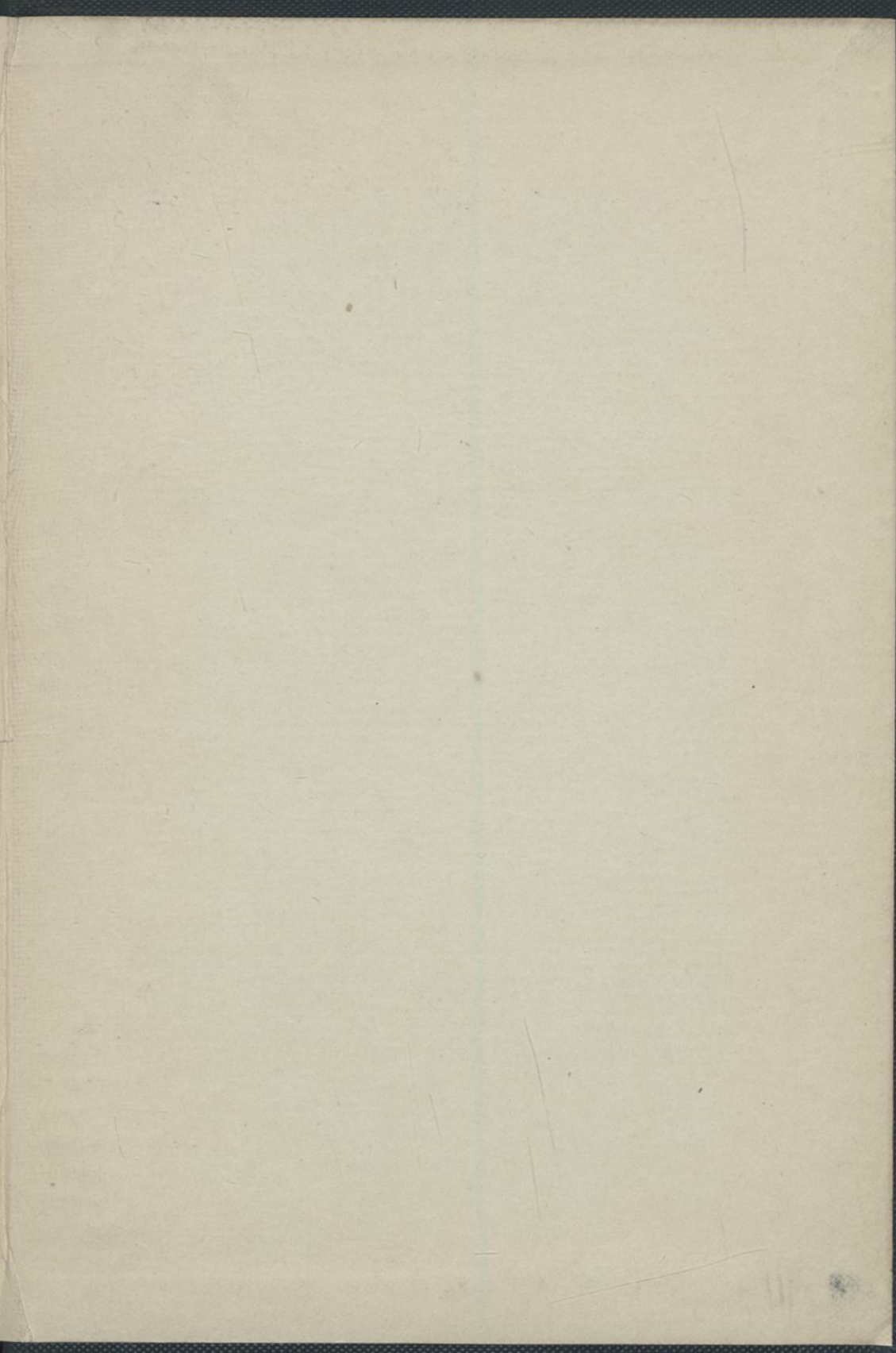
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