MARIN R. MEHANDIJEV*, GEORGI RUSSEV*, ZDRAVKO DINEV*

APPLICATION OF ACCUMULATION THERMODYNAMICS REGULARITIES IN THE STRIPPING OF ORGANIC POLLUTANTS FROM WASTEWATERS BY RADIATION-ACTIVATED POLYMERIZATION

An application of thermodynamics of accumulation processes (TAP) to prediction of effects of some wastewater treatment processes, e.g. adsorption of soluble impurities on precipitate surfaces, has been presented. It has been proved theoretically that the fast precipitate formation should ensure an additional adsorption effect. This hypothesis has been confirmed by experimental study on organic pollutant adsorption on precipitates formed in the gamma radiation-activated polymerization of some monomers (i.e. methylmetacrylate) added purposely to the wastewater. The results obtained can be used in design a new economic method of wastewater treatment.

Accumulation thermodynamics or thermodynamics of accumulation processes (TAP) [1–3] deals with the phenomena of accumulation in affected, non-isolated — open or closed — systems. The thermodynamic potential G (e.g. the Gibbs free energy) of an affected system increases due to the work done on the system by external impacts during the accumulation time τ.

The thermodynamic potential and other functions of state of the system can be defined (eq. 1) as the sum of n various elementary kinds of energy E_k, existing or appearing in the affected system. This is equal to the sum of the products of the appropriate thermodynamic conjugates P_k and X_k

$$G = \sum_{k=1}^{n} E_k = \sum_{k=1}^{n} P_k X_k \quad (k = 1, 2, 3, \ldots, n), \tag{1}$$

where P_k and X_k are intensive and extensive properties of state, respectively.

The conjugation between each pair (P_k, X_k), based on the canonical theory of equations, has been called a "monoenergetic conjugation", since the variables represent a single elementary kind of energy.

* Sofia, Bulgaria.

TAP distinguishes two types of effects in the affected ("in-") systems due to impacts originating from external ("ex-") systems, i.e.:

a) direct (homoenergetic) effects, occurring through changes in properties which represent the same elementary kinds of energy as the driving forces (e.g. $dT_{in} > 0$ is the direct effect of a heat impact; the temperature difference $\Delta T = T_{ex} - T_{in}$ is the driving force of the impact),

b) indirect (heteroenergetic) effects, occurring through changes in properties of state different from those representing the driving forces (e.g. $dT_{in} > 0$ in a gaseous system is an indirect effect of pressure increase).

According to the TAP-rule the polyenergetization of effects in the affected system and each impact, even the one including a single driving force, results in two energetic effects. TAP assumes also that the bound energy G_S is such a part of the system internal energy which can be changed only by indirect effects or by changes in extensive variables, being homoenergetic to the driving forces of the impact.

A relationship (2) called a polyenergetic conjugation, existing between the intensive and extensive variables of state, associates factors defining different elementary kinds of energy:

$$T \prod_{r=1}^{j} P_r \pm \bar{\Theta}_r \prod_{i=j+1}^{n-1} X_i \pm \bar{\Theta}_i = \text{const}, \quad (r+i+1 = n \geqslant 2), \tag{2}$$

where $\bar{\Theta}_r$ and $\bar{\Theta}_i$ are relative exponents less than 1, while the exponent of the temperature T is assumed to equal 1. The equation of polyenergetic conjugation (2) has been derived for the impacts with "compensated" effects in the in-system and without mass action. The impacts can also be accompanied with a qualitative transformation of the effects which can be realized in the appearance of new or disappearance of the existing kinds of energy in the affected system, respectively. The state of compensated effects is the result of a full correspondence between the direct and indirect effects, causing an "internal zeroing" of the introduced free energy. Such states of a full conformity of effects are denoted by $dG = - dG_S$ or by $\overline{dG = -dG_S}$, since the "compensation" of the changes of the free thermodynamic potential and of the bound energy in the system expresses generally the correspondence of the changes of separate variables in those cases. So an action with compensated effects without mass action is denoted by $\overline{dG = -dG_S}$, $dm = 0$. There exist several possibilities for the compensation of the effects: a) all homo- and heteroenergetic effects can be totally accumulated; b) the heteroenergetic effects can be fully accumulated in the system; c) all the effects can be accumulated in the system, initially as bound energy changes only. In all the cases, the criterion for the compensation of effects is the complete accumulation of all heteroenergetic effects. The gaseous adiabatic system is an example of the simplest system accumulating completely the energy introduced during the impact. The process of full accumulation of the action energy can always be realized by a sufficiently fast impact upon any system, even if the complete accumulation is a temporary one. During this operation such systems have been treated as "kinetically-adiabatic systems".

The equilibrium thermodynamics accepted the heat effects as universal appearance of bound energy change dG_S in the affected systems. If the TAP-rule of the polyenergetization of effects in the in-systems is taken into account, then the change of a single elementary kind of energy for dG_S-realization cannot be accepted, for the question about the dG_S-appearance in the cases of pure heat impact (heat introduced as a single impact, hence ΔT = driving force) in the affected systems, especially in liquid and/or solid systems, remains without answer. Using the TAP-definition for the bound energy, it was easy to select the surface energy as a more universal elementary kind of energy for the appearance of bound energy than the heat effect, since the surface energy effects can only be heteroenergetic (impacts or interactions between systems caused only by the differences of surface tension as driving forces are unfeasible). Therefore, the polyenergetic conjugation associating the temperature and the extensive factor of the surface energy — the surface area s — has been considered.

The relative exponents of P_r and X_i in (2) prove to be approximately constant: $\bar{\Theta}_r \equiv \Theta_r \approx 0.3$, $\bar{\Theta}_i \equiv \Theta_i \approx 0.4$ in expressions for effects without qualitative transformation. Those theoretically estimated and experimentally verified relative exponent values are independent of the number of the variables in (2) as well as of the effect sign (positive or negative effects). The polyenergetic conjugation for crystallization effects without qualitative transformation (cooling saturated liquors after seeding the crystals, i.e. under conditions of a predominant growth of crystal surfaces) is given by equation (3)

$$Ts^{\Theta_i}V^{\Theta_i} = \text{const} \quad (n = 3, \ \overline{dG = -dG_S}, \ dm = 0), \tag{3}$$

where S is the surface area of crystals and V is the volume of mother liquor.

The following salts have been used in the crystallization experiments: $Al_2(SO_4)_3 \cdot 18\,H_2O$, $MnSO_4 \cdot H_2O$, $Na_2SO_4 \cdot 10\,H_2O$, $CaHPO_4 \cdot 2\,H_2O$, $(NH_4)_2HPO_4$, KH_2PO_4, $NaH_2PO_4 \cdot 2\,H_2O$, $Na_3PO_4 \cdot 12H_2O$, and $Na_4P_2O_7 \cdot 10H_2O$. The corresponding values of the exponents in (3), each obtained by 54 or 60 calculations, are as follows: 0.386 ± 0.057, 0.411 ± 0.093, 0.382 ± 0.089, 0.392 ± 0.048, 0.401 ± 0.063, 0.409 ± 0.071, 0.410 ± 0.083, 0.398 ± 0.017, and 0.398 ± 0.042 [4, 5]. The well-known adiabatic equation for gases: $T \cdot v^{\varkappa-1} = \text{const}$ can be accepted as a particular case of (2) for $n = 2$, since $\varkappa - 1 \equiv \Theta_i \approx 0.4$ for most gases.

For the effects accompanied with the qualitative transformation, the values of relative exponent in (2) vary with the kind of energy, but they do not vary with the sign of effect. The equation (4) was used for qualitative transformation of crystallization effects created when a new solid phase is formed predominantly in the system (cooling saturated liquors without seeding):

$$T \cdot s^{\psi_s} = \text{const} \quad (n = 2, \ \overline{-dG = dG_S}, \ dm = 0). \tag{4}$$

The mean values of the surface area exponent ψ_s, obtained using the same compounds as before, range from 0.039 ± 0.005 to 0.041 ± 0.004 [5], indicating a good conformity with the surface area exponent value (0.04) calculated on a base of electrocrystallization data

[6]. The mean value of ψ_s in (4) calculated from Nyvlt results [7] (crystallization of $Ca(NO_3)_2 \cdot 4\ H_2O$, 14 calculations) is 0.0414 as well.

From equation (2), an important conclusion can be drawn for the wastewater treatment process using large-surface-precipitates for adsorption of soluble impurities. Substituting the adsorption tension I_a and the precipitate surface area s to eq. (2) and differentiating it with respect to the time τ for $h = 2$ and $T = $ const, we obtain equation (5):

$$\frac{\bar{\Theta}_a dI_a}{I_a d\tau} = \frac{\bar{\Theta}_s ds}{s d\tau}. \tag{5}$$

From (5) we conclude that a fast precipitate formation will ensure an additional adsorption effect, since the rates in (5) are antibatic and since I_a decreases with the increasing quantity of the adsorbate g. This conclusion was proved experimentally in the case of organic pollutants adsorption by means of precipitates formed in the gamma radiation-activated polymerization of monomers (e.g. methylmetacrylate — MMA) added to the industrial wastewater to be treated.

Exposing the wastewater samples (constant initial concentration of polutant) to a constant radiation of total energy of 0.3 Mrad and applying various radiation intensities $dV/d\tau = q$ (Mrad/h) as well as various times of exposition $\tau(h)$, we have obtained the values of pollutant adsorption rate $dg/d\tau = w$ (mg/h). Each experiment was repeated three times and the mean values of W were calculated (table).

Table

Mean values of pollutant adsorption rate $dg/d\tau = w$ (mg/h) in radiation-activated MMA-polymerization process at various radiation intensities $dY/d\tau = q$ (Mrad/h) and exposition time τ (h). (Radiation quantity $= 0.3$ Mrad $=$ const in each test)

Średnie wartości szybkości adsorpcji polutanta $dg/d\tau = w$ (mg/h) dla MMA-polmeryzacji pobudzonej przez promieniowanie przy różnych intensywnościach $dY/d\tau = q$ (Mrad/h) i czasie τ(h) promieniowania. (0,3 Mrad $=$ const w każdym doświadczeniu)

	q Mrad/h	0.025	0.070	0.228	0.600
	τ, h	12	4.286	1.316	0.5
MMA-concentration in wastewater	Test no.	1	2	3	4
0.2	A	0.007	0.02006	0.066	0.174
0.3	B	0.007	0.02009	0.0663	0.1746
0.5	C	0.007	0.02004	0.066	0.174
0.7	D	0.007	0.02002	0.0663	0.174

The results in table prove directly the conclusion stated above. They present, moreover, a new possibility of Θ_i-value veryfying as well as a new possibility of TAP-regularities corroboration.

Since the rate $ds/d\tau$ is proportional to $dV/d\tau$ and $dg/d\tau$ is reverse proportional to $dI_a/d\tau$, then from (5) the calculating equation (6) can be derived:

$$\frac{0.4}{q_m}(q_x - q_y) = \frac{\Theta_g}{w_m}(w_x - w_y), \qquad (6)$$

where x and y $(x > y)$ are the double test numbers: $(A1, \ldots, A4), (B1, \ldots, B4), (C1, \ldots, C4)$, and $(D1, \ldots, D4)$ for each MMA-concentration in table; q_m and w_m are mean values:

$$q_m = \frac{q_x + q_y}{2}, \qquad w_m = \frac{w_x + w_y}{2}.$$

The calculations employing all the 24 possible equations of (6)-type gave the value 0.4 ± 0.0002 for Θ_g, being in a full coincidence with the theoretical evaluations and also with the previous values.

The important practical conclusion from (5) and its experimental proof have been used in our research work for selection of an economically effective wastewaters treatment.

REFERENCES

[1] MEHANDIJEV M. R., *Essay on Dissertation*, High Chem. Techn. Inst. "A. Zlatarov", Burgas 1969 (Bulg.).
[2] MEHANDIJEV M. R., MEHANDIJEVA K. R., Paper of II Conf. Rep. on Physical Chemistry, Proceed. Vol. II, p. 138, Bucharest 1970.
[3] MEHANDIJEV M. R., GRAMATIKOV M. W., Tsv. Obretenov, Wiss. Zeitsch. Techn. Hochsch. Chem., Leuna-Merseburg, Vol. 14 (1972), p. 110.
[4] MEHANDIJEV M. R., Abstr. vol. of 8th Exper. Thermodyn. Conference, Guildford 1978, p. 46.
[5] MEHANDIJEV M. R., Abstr. vol. of Internat. Conference on Phosphorus Chemistry, Halle 1979, p. 213.
[6] MEHANDIJEV M. R., MEHANDIJEVA K. R., Metalloberflache, Vol. 28 (1974), No. 3, p. 88.
[7] NYVLT J., *Krystalizacia z roztokov*, Slov. vyd. techn. lit., Bratislava 1967.

ZASTOSOWANIE TERMODYNAMIKI PROCESÓW AKUMULACYJNYCH DO USUWANIA ZANIECZYSZCZEŃ ORGANICZNYCH ZE ŚCIEKÓW PRZY UŻYCIU POLIMERYZACJI WYWOŁANEJ PROMIENIOWANIEM

Przedstawiono zastosowanie termodynamiki procesów akumulacyjnych (TAP) w przewidywaniu efektów niektórych procesów oczyszczania ścieków, np. adsorpcji rozpuszczalnych zanieczyszczeń na powierzchni osadów. Wykazano teoretycznie, że szybkie formowanie się osadów powinno wywołać dodatkowy efekt adsorpcyjny. Badania eksperymentalne adsorpcji zanieczyszczeń organicznych na osadach powstałych w wyniku polimeryzacji niektórych monomerów (np. metakrylanu metylu), celowo dodanych do ścieków, potwierdziły przewidywania teoretyczne. Uzyskane wyniki mogą stanowić podstawę opracowania nowej, ekonomicznie opłacalnej metody oczyszczania ścieków.

THERMODYNAMIK DER AKKUMULATIONSPROZESSE BEI DER BESEITIGUNG VON ORGANISCHEN VERUNREINIGUNGEN AUS DEM ABWÄSSER MIT HILFE DER DURCH STRAHLUNG VERURSACHTEN POLYMERISATION

Dargestellt wird die Anwendung der Thermodynamik der Akkumulationsprozesse (TAP) in der Voraussicht der Resultate mancher Abwasserreinigungsverfahren wie z.B. der Adsorption von gelösten Verunreinigungen auf der Oberfläche von Schlammpartikeln. Theoretisch wurde erwiesen, daß eine beschleunigte Schlammbildung einen zusätzlichen Adsorptionseffekt bewirken müßte. Experimente zur Adsorption von organischen Verunreinigungen auf Schlämmen, die als Folge einer Polymerisation von Monomeren (z.B. von Methylmetakrylan) entstanden sind und zielbewusst dem Abwasser zugegeben wurden, bestätigten die theoretischen Erwägungen. Die erzielten Resultate können eine Basis für ein neues, wirksames und wirtschaftliches Abwasserreinigungsverfahren sein.

ПРИМЕНЕНИЕ ТЕРМОДИНАМИКИ АККУМУЛЯЦИОННЫХ ПРОЦЕССОВ В УДАЛЕНИИ ОРГАНИЧЕСКИХ ЗАГРЯЗНЕНИЙ ИЗ СТОЧНЫХ ВОД ПРИ ИСПОЛЬЗОВАНИИ ПОЛИМЕРИЗАЦИИ, ВЫЗВАННОЙ ИЗЛУЧЕНИЕМ

Представлено применение термодинамики аккумуляционных процессов (ТАП) при предвидении эффектов некоторых процессов очистки сточных вод, например, адсорбции растворимых загрязнений на поверхности осадков. Теоретически доказано, что быстрое формирование осадков должно вызвать дополнительный адсорбционный эффект. Экспериментальные испытания адсорбции органических загрязнений на осадках, образовавшихся в результате полимеризации некоторых мономеров (например, метилметакрилата), преднамеренно добавленных к сточным водам, подтвердили теоретические предвидения. Полученные результаты могут представлять собой основу разработки нового экономически выгодного метода очитки сточных вод.