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Elovich-Type Equations for Description of the Adsorption Rates of Gas Mixtures

In adsorption kinetics the Elovich equations describing the adsorption and desorption rates of single gases are very popular; many experimental data fit these relationships. Usually, they are written in the form:

$$R^{\mathrm{a}} = d\theta/dt = A \exp(-\alpha\theta/RT) \quad \text{(1a)}$$

and

$$R^{\mathrm{d}} = -d\theta/dt = B \exp(\beta\theta/RT), \quad \text{(1b)}$$

where R^{a} and R^{d} are rates of adsorption and desorption, respectively, and θ is the monolayer surface coverage. The constant α (β) is the parameter defining the relationship between the activation energy of adsorption, E^{a} (activation energy of desorption, E^{d}) and the surface coverage θ, i.e.,

$$E^{\mathrm{a}} = \hat{E}^{\mathrm{a}} + \alpha\theta \quad \text{(2a)}$$

and

$$E^{\mathrm{d}} = \hat{E}^{\mathrm{d}} - \beta\theta. \quad \text{(2b)}$$

However, the constants A and B are given by the following equations:

$$A = \frac{RT\hat{k}^{\mathrm{a}}p}{\alpha} \exp(-\hat{E}^{\mathrm{a}}/RT) \quad \text{(3a)}$$

and

$$B = \frac{RT\hat{k}^{\mathrm{d}}}{\beta} \exp(-\hat{E}^{\mathrm{d}}/RT), \quad \text{(3b)}$$

where p is the adsorbate pressure, and $\hat{k}^{\mathrm{a}}$ and $\hat{k}^{\mathrm{d}}$ are constants of adsorption and desorption, respectively. Assuming the linear functions (2a) and (2b), which generates a linear relationship between adsorption energy, ϵ, and surface coverage, θ,

$$\epsilon = \epsilon^{\mathrm{M}} - \gamma\theta; \quad \text{(4)}$$

the Elovich equations (1a) and (1b) may be obtained by means of the following integrals (*1*):

$$R^{\mathrm{a}} = \int_{\Delta} (1 - \Theta)\hat{k}^{\mathrm{a}}p \times \exp(-E^{\mathrm{a}}/RT)\chi(\epsilon)d\epsilon \quad \text{(5a)}$$

and

$$R^{\mathrm{d}} = \int_{\Delta} \Theta\hat{k}^{\mathrm{d}} \exp(-E^{\mathrm{d}}/RT)\chi(\epsilon)d\epsilon \quad \text{(5b)}$$

with the stepwise local kinetic isotherm $\Theta(\epsilon)$:

$$\begin{aligned} \Theta(\epsilon) &= 0 \quad \text{for} \quad \epsilon \leqslant \epsilon^{*} \\ &= 1 \quad \text{for} \quad \epsilon > \epsilon^{*} \end{aligned} \quad \text{(6)}$$

and the constant energy distribution $\chi(\epsilon)$:

$$\chi(\epsilon) = [\epsilon^{\mathrm{M}} - \epsilon^{\mathrm{m}}]^{-1} = c. \quad \text{(7)}$$

Relationship (4) may be obtained from the integral adsorption isotherm:

$$\theta = \int_{\Delta} \Theta(\epsilon)\chi(\epsilon)d\epsilon \quad \text{(8)}$$

with the subintegral functions (6) and (7). In the above, ϵ^{M} and ϵ^{m} are maximum and minimum values of ϵ, and γ is a constant expressed by means of ϵ^{M} and ϵ^{m}.

In this note the Elovich-type equations for description of the adsorption and desorption rates of n-component gas mix-

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tures are derived by using a general theory of mixed-gas adsorption on heterogeneous solid surfaces (*2–4*). First, the Elovich-type equation for adsorption rate of the ith component, $R_{i(\mathbf{n})}{}^{\mathrm{a}}$, will be derived by using the integral

$$R_{i(\mathbf{n})}{}^{\mathrm{a}} = \int_{\Delta(\mathbf{n})} (1 - \sum_{i=1}^{n} \Theta_{i(\mathbf{n})})\hat{k}_i{}^{\mathrm{a}} p_i \times \exp(-E_i{}^{\mathrm{a}}/RT)\chi_{(\mathbf{n})}(\boldsymbol{\varepsilon})d\boldsymbol{\varepsilon}, \quad (9)$$

where $\Theta_{i(\mathbf{n})}$ is the monolayer surface coverage for adsorption of the ith component from an n-component gas mixture; $\boldsymbol{\varepsilon} = (\epsilon_1, \epsilon_2, \ldots, \epsilon_n)$, and $\mathbf{n} = (1, 2, \ldots, n)$ are n-dimensional vectors; $\chi_{(\mathbf{n})}$ is n-dimensional energy distribution, which is normalized to unity:

$$\int_{\Delta(\mathbf{n})} \chi_{(\mathbf{n})}(\boldsymbol{\varepsilon})d\boldsymbol{\varepsilon} = 1, \quad (10)$$

where $\Delta_{(\mathbf{n})}$ is n-dimensional integration region defined by

$$\Delta_{(\mathbf{n})} = (\epsilon_1{}^{\mathrm{m}}, \epsilon_1{}^{\mathrm{M}}) \times (\epsilon_2{}^{\mathrm{m}}, \epsilon_2{}^{\mathrm{M}}) \times \cdots \times (\epsilon_n{}^{\mathrm{m}}, \epsilon_n{}^{\mathrm{M}}). \quad (11)$$

Eq. (9) describes the adsorption rate at low surface coverages; then the monolayer adsorption is dominant. Although Eq. (9) limits theoretical discussion to low surface coverages, our results are important from the viewpoint of adsorption kinetics on energetically heterogeneous solid surfaces. The heterogeneity effects play an important role at the beginning of the adsorption process. In Eq. (9) the global heterogeneity of the adsorbent surface is taken into account by means of an n-dimensional energy distribution $\chi_{(\mathbf{n})}(\boldsymbol{\varepsilon})$. For this function different n-dimensional distributions may be assumed. In such a treatment every adsorption site on the heterogeneous surface is characterized by n adsorption energies: ϵ_1, ϵ_2, …, and ϵ_n; where ϵ_i ($i = 1, 2, \ldots, n$) is the adsorption energy characterizing the interaction of a given adsorption site with one molecule of the ith component. The Elovich-type equation for the adsorption rate of an n-component gas mixture may be obtained from Eq. (9), if the n-dimensional constant energy distribution (*3*):

$$\chi_{(\mathbf{n})}(\boldsymbol{\varepsilon}) = \prod_{i=1}^{n} [\epsilon_i{}^{\mathrm{M}} - \epsilon_i{}^{\mathrm{m}}]^{-1} = c_{(n)} \quad (12)$$

and the stepwise local kinetic isotherm:

$$\begin{aligned} \Theta_{i(\mathbf{n})} &= 0 \quad \text{for} \quad \boldsymbol{\varepsilon} \leqslant \boldsymbol{\varepsilon}^* \\ &= 1 \quad \text{for} \quad \boldsymbol{\varepsilon} > \boldsymbol{\varepsilon}^* \end{aligned} \quad (13)$$

are applied for $\chi_{(\mathbf{n})}(\boldsymbol{\varepsilon})$ and $\Theta_{i(\mathbf{n})}$, respectively. Application of Eq. (12) for $\chi_n(\boldsymbol{\varepsilon})$ means that the adsorption energies for the various adsorbates are uncorrelated. Moreover, assumption of Eq. (13) for $\Theta_{i(\mathbf{n})}$ is equivalent to the assumption of the so-called "condensation approximation" (*6*), which can be applied to surface whose distributions have a spread much more than RT (*6*). Thus, Eqs. (12) and (13) mainly limit the applicability of the Elovich-type equations for description of adsorption rates.

Applying Eqs. (12) and (13) in the integral equation for the overall adsorption isotherm, $\theta_{i(\mathbf{n})}$, i.e.,

$$\theta_{i(\mathbf{n})} = \int_{\Delta(\mathbf{n})} \Theta_{i(\mathbf{n})}(\boldsymbol{\varepsilon})\chi_{(\mathbf{n})}(\boldsymbol{\varepsilon})d\boldsymbol{\varepsilon} \quad (14)$$

we obtain the relationships between $\theta_{i(\mathbf{n})}$ and ϵ_i for all ϵ_i, they are:

$$\theta_{i(\mathbf{n})} = \prod_{i=1}^{n} (\epsilon_i{}^{\mathrm{M}} - \epsilon^*{}_i)/(\epsilon_i{}^{\mathrm{M}} - \epsilon_i{}^{\mathrm{m}}) \quad \text{for } i = 1, 2, \ldots, n. \quad (15)$$

After omitting the upper index of $\epsilon_i{}^*$, the equations system (15) may be presented in the form:

$$\epsilon_i = \hat{\epsilon}_i - \sum_{j=1}^{n} \gamma_{ij}\theta_{j(\mathbf{n})} \quad \text{for } i = 1, 2, \ldots, n, \quad (16)$$

where the matrix D of this transformation satisfies the following condition:

$$\det D = \begin{vmatrix} \gamma_{11}^* & \gamma_{12}^* & \cdots & \gamma_{1n}^* \\ \gamma_{21}^* & \gamma_{22}^* & \cdots & \gamma_{2n}^* \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \gamma_{n1}^* & \gamma_{n2}^* & \cdots & \gamma_{nn}^* \end{vmatrix} \neq 0;$$

$$\gamma_{ij}^* = -\gamma_{ij}. \quad (17)$$

Now define the relationship between E_i^{a} and $\theta_{i(\mathrm{n})}$:

$$E_i^{\mathrm{a}} = \hat{E}_i^{\mathrm{a}} + \sum_{j=1}^{n} \alpha_{ij}\theta_{j(\mathrm{n})}; \qquad \det[\alpha_{ij}] \neq 0$$

$$\text{for } i = 1, 2, \ldots, n. \quad (18)$$

This relationship has been defined in a similar way to that given by Eq. (16). Substituting Eqs. (12), (13), and (18) into Eq. (9) and transforming variables by means of Eq. (16), we have

$$\begin{aligned} R_{i(\mathrm{n})}^{\mathrm{a}} &= c_{(\mathrm{n})}\hat{k}_i^{\mathrm{a}} p_i \exp(-\hat{E}_i^{\mathrm{a}}/RT) \\ &\quad \cdot J \cdot \prod_{j=1}^{n} \int_{\theta_{j(\mathrm{n})}}^{1} \exp\left(\frac{-\alpha_{ij}\theta_{j(\mathrm{n})}}{RT}\right) d\theta_{j(\mathrm{n})} \\ &= c_{(\mathrm{n})}\hat{k}_i^{\mathrm{a}} p_i \exp(-\hat{E}_i^{\mathrm{a}}/RT) \\ &\quad \cdot J \cdot \prod_{j=1}^{n} \left\{ \frac{RT}{\alpha_{ij}} \left[\exp\left(\frac{-\alpha_{ij}\theta_{j(\mathrm{n})}}{RT}\right) \right.\right. \\ &\quad \left.\left. - \exp\left(\frac{-\alpha_{ij}}{RT}\right) \right] \right\}, \end{aligned}$$

$$\text{where } J = \det D \quad (19)$$

Taking into account the following inequality in Eq. (19),

$$\exp\left(\frac{-\alpha_{ij}\theta_{j(\mathrm{n})}}{RT}\right) \gg \exp\left(\frac{-\alpha_{ij}}{RT}\right)$$

$$\text{for } \theta_{j(\mathrm{n})} \ll 1, \quad (20)$$

we obtain the Elovich-type equation for the description of the adsorption rate of the ith component from the n-component gas mixture:

$$R_{i(\mathrm{n})}^{\mathrm{a}} = A_i \exp\left(\frac{-1}{RT} \sum_{j=1}^{n} \alpha_{ij}\theta_{j(\mathrm{n})}\right)$$

$$\text{for } i = 1, 2, \ldots, n, \quad (21)$$

where

$$A_i = c_{(\mathrm{n})}\hat{k}_i^{\mathrm{a}} p_i \exp(-\hat{E}_i^{\mathrm{a}}/RT) \cdot J \cdot \prod_{j=1}^{n} \left(\frac{RT}{\alpha_{ij}}\right). \quad (22)$$

By means of rearrangements very similar to the above we can obtain the equation for the desorption rate of the ith component from the n-component gas mixture:

$$\begin{aligned} R_{i(\mathrm{n})}^{\mathrm{d}} &= c_{(\mathrm{n})}\hat{k}_i^{\mathrm{d}} \exp(-\hat{E}_i^{\mathrm{d}}/RT) \\ &\quad \cdot J \cdot \prod_{j=1}^{n} \int_{0}^{\theta_{j(\mathrm{n})}} \exp\left(\frac{\beta_{ij}\theta_{j(\mathrm{n})}}{RT}\right) d\theta_{j(\mathrm{n})} \\ &= c_{(\mathrm{n})}\hat{k}_i^{\mathrm{d}} \exp(-\hat{E}_i^{\mathrm{d}}/RT) \\ &\quad \cdot J \cdot \prod_{j=1}^{n} \left\{ \frac{RT}{\beta_{ij}} \left[\exp\left(\frac{\beta_{ij}\theta_{j(\mathrm{n})}}{RT}\right) - 1 \right] \right\}, \end{aligned} \quad (23)$$

where

$$E_i^{\mathrm{d}} = \hat{E}_i^{\mathrm{d}} - \sum_{j=1}^{n} \beta_{ij}\theta_{j(\mathrm{n})}. \quad (24)$$

Taking into account the following initial condition,

$$\exp\left(\frac{\beta_{ij}\theta_{j(\mathrm{n})}}{RT}\right) \gg 1 \qquad \text{for } \theta_{j(\mathrm{n})} > 0, \quad (25)$$

we have

$$R_{i(\mathrm{n})}^{\mathrm{d}} = B_i \exp\left(\frac{1}{RT} \sum_{j=1}^{n} \beta_{ij}\theta_{j(\mathrm{n})}\right)$$

$$\text{for } i = 1, 2, \ldots, n. \quad (26)$$

The constant B_i is expressed by

$$B_i = c_{(\mathrm{n})}\hat{k}_i^{\mathrm{d}} \exp(-\hat{E}_i^{\mathrm{d}}/RT) \cdot J \cdot \prod_{j=1}^{n} \left(\frac{RT}{\beta_{ij}}\right). \quad (27)$$

Eq. (9) for $R_{i(\mathrm{n})}^{\mathrm{a}}$ and the equation

$$R_{i(\mathrm{n})}^{\mathrm{d}} = \int_{\Delta(\mathrm{n})} \Theta_{i(\mathrm{n})}\hat{k}_i^{\mathrm{d}} \times \exp(-E_i^{\mathrm{d}}/RT)\chi_{(\mathrm{n})}(\boldsymbol{\varepsilon})d\boldsymbol{\varepsilon} \quad (28)$$

for $R_{i(\mathrm{n})}{}^{\mathrm{d}}$ have general forms; using different equations for and $\chi_{(\mathrm{n})}$ we can obtain different analytical approximations for $R_{i(\mathrm{n})}{}^{\mathrm{a}}$ and $R_{i(\mathrm{n})}{}^{\mathrm{d}}$.

It has been shown that the Elovich-type equations (21) and (26) of adsorption and desorption rates of the ith component from an n-component gas mixture may be easily derived by using the treatment presented by the author in previous papers (*2–4*). Very similar equations to Eqs. (21) and (26) have been proposed by De Boer (*5*) for binary gas mixtures. According to De Boer's treatment, the relationships between ϵ_i and $\theta_{j(\mathrm{n})}$, $E_i{}^{\mathrm{a}}$ and $\theta_{j(\mathrm{n})}$, $E_i{}^{\mathrm{d}}$ and $\theta_{j(\mathrm{n})}$ (for $j = 1, 2, \cdots, n$) are given by equations of the type (16), (18), and (24) with the following additional assumptions:

$$\gamma_{ij} = \gamma_j; \quad \alpha_{ij} = \alpha_j; \quad \beta_{ij} = \beta_j \quad \text{for} \quad i = 1, 2, \ldots, n. \qquad (29)$$

It follows from the presented derivation of Eqs. (21) and (26) that such assumptions give $\det D = \det[\alpha_{ij}] = \det[\beta_{ij}] = 0$ and then $R_{i(\mathrm{n})}{}^{\mathrm{a}}$, $R_{i(\mathrm{n})}{}^{\mathrm{d}}$ are also equal to zero.

REFERENCES

1. Fejes, P., *in* "Contact Catalysis" (Z. G. Szabó and D. Kalló, Eds.), Vol. 1, pp. 221–228. Akadémiai Kiado, Budapest, 1976.

2. Jaroniec, M., *J. Chem. Soc. Faraday II* **73**, 933 (1977).

3. Jaroniec, M., *J. Colloid Interface Sci.* **53**, 422 (1975).

4. Jaroniec, M., *J. Chem. Soc. Faraday II* **74**, 1292 (1978).

5. De Boer, J. H., *Advan. Catal.* **8**, 141 (1956).

6. Cerofolini, G. F., *Thin Solid Films* **23**, 129 (1974).

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