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SOLUTION THERMODYNAMICS OF ADSORPTION IN MICROPOROUS ADSORBENTS

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From the conception that the adsorption process in microporous solids consists in a volumetric filling of an adsorption space and the formation of a monophasic system (adsorbate-adsorbent) as is the case in solutions, and with the use of solution thermodynamics, expressions were obtained for the well-known isosteric heat of adsorption, the enthalpy of adsorption and the differential heat of adsorption, and non-trivial relations were then established between these thermodynamic magnitudes.

Microporous solids are solids in which the diameters of the adsorption channels are comparable to the diameters of the adsorbed molecules, as is the case for molecular sieves, many activated charcoals, some silica gels, alumina gels, ceramics, etc. This means that there is a qualitative difference from adsorption in macroporous or non-porous adsorbents, due to the fact that adsorption in microporous solids is not a surface process, but a *volume filling*.

The thermodynamics of adsorption and solution thermodynamics for surfaces have been well treated by Gibbs, Hill, Everett and others [1–5]. On the other hand, Dubinin, Serpinskii and Bering [6–12] have dealt with the thermodynamics of adsorption in microporous solid adsorbents in recent years, within the theory of volume filling.

In the present paper, from the conception of adsorption as the volumetric filling of an adsorption space, with the formation of a monophasic system (adsorbate-adsorbent (aA)) during adsorption, as is the case in solutions, expressions have been obtained for the well-known isosteric heat of adsorption, the enthalpy of adsorption and the differential heat of adsorption, and non-trivial relations have been established between these thermodynamic magnitudes.

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Isosteric heat of adsorption and partial molar enthalpy of adsorption

According to the theory of volume filling, the system is a monophasic one, comparable with a homogeneous solution of adsorbate molecules in a solid adsorbent. For this system the fundamental thermodynamic equation [13] is:

$$\mathrm{d}E_{aA} = T\mathrm{d}S_{aA} - P\mathrm{d}V_{aA} + \mu_a \mathrm{d}n_a + \mu_A \mathrm{d}n_A \qquad (1)$$

where E_{aA}, and S_{aA} and V_{aA} are the internal energy, entropy and volume of the system aA and μ_a, μ_A and n_a, n_A are the chemical potentials and the number of moles of adsorbate and adsorbent in the system aA.

With the definition $\Gamma = n_a/n_A$, we have $\mu_a = \mu_a(T, P, \Gamma)$ and $\mu_A = \mu_A(T, P, \Gamma)$. In this case:

$$\mathrm{d}\mu_a = \overline{S}_a \mathrm{d}T + \overline{V}_a \mathrm{d}P + \left(\frac{\partial \mu_a}{\partial \Gamma}\right)_{T,P} \mathrm{d}\Gamma \qquad (2)$$

where $\overline{S}_a$ and $\overline{V}_a$ are the partial molar entropy and volume of the adsorbate in the system aA. As the system aA must be in equilibrium with a gas phase of adsorbate molecules which fulfils the relation:

$$\mathrm{d}\mu_g = \overline{S}_g \mathrm{d}T + \overline{V}_g \mathrm{d}P$$

it is possible to show (considering the gase phase as ideal) that for Γ = const.:

$$\left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right) = \frac{\overline{H}_g - \overline{H}_a}{RT^2} \qquad (3)$$

where $\overline{H}_g$ and $\overline{H}_a$ are the partial molar enthalpies of the adsorbate in the gas phase in the system aA.

By definition, on the other hand, the isosteric heat of adsorption is:

$$\left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right)_\Gamma = \frac{q_{\mathrm{iso}}}{RT^2} \qquad (4)$$

and consequently $q_{\mathrm{iso}} = \overline{H}_g - \overline{H}_a$.

It is possible to show [11, 13] that:

$$\Phi = -(\mu_A - \mu_A^0) = RT\int_0^P \Gamma \,\mathrm{d}\ln P$$

in which μ_A^0 is the chemical potential of the adsorbent completely empty of adsorbate. In this case it is possible that $\mu_a = \mu_a(P, T, \Phi)$ and it is easy to show that, for Φ = const.:

$$\left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right)_\Phi = \frac{\overline{H}_g - \overline{H}_e}{RT^2} \qquad (5)$$

where $\bar{H}_g - \bar{H}_e \doteq (\bar{S}_g - \bar{S}_e)\, T$ and $\bar{S}_e = -\left(\frac{\partial \mu_a}{\partial T}\right)_{P,\Phi}$. Since by definition the partial molar enthalpy of adsorption [4] is:

$$\left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right)_{\Phi} = \frac{(-\Delta \bar{H}_{\mathrm{ads}})}{RT^2}$$

we have $(-\Delta \bar{H}_{\mathrm{ads}}) = \bar{H}_g - \bar{H}_e$.

Differential heat of adsorption

We define an adsorption experiment [5] taking place in an isolated system of a thermostat of infinite capacity, and an adsorption apparatus, where there are n moles of adsorbate, initially at a pressure P_i in the volume V_d of the adsorption apparatus, and this is allowed to come into contact isothermally with n_A moles of adsorbent in a vessel connected with V_d, adsorption continuing till equilibrium is reached at a final pressure P_f. The total energy of the overall system (thermostat plus adsorption apparatus) is initially:

$$E_T^i = E_1 + nE_g + n_A E_A^0 \tag{7}$$

where E_1 is the thermostat energy, E_g is the molar energy of the adsorbate in the gaseous state, and E_A^0 is the molar energy of the empty adsorbent (i.e. without adsorbate molecules in the adsorption space of the solid adsorbent).

The final energy of the system is:

$$E_T^f = E_2 + (n - n_a)\bar{E}_g + n_A \bar{E}_A + n_a \bar{E}_a \tag{8}$$

where n_a is the number of moles adsorbed, $\bar{E}_a$ is the partial molar energy of the adsorbate in the system aA and $\bar{E}_A$ is the partial molar energy of the adsorbent in the system aA.

By definition:

$$E_T^i = E_T^f$$

Therefore:

$$E_2 - E_1 = n_a \bar{E}_g - n_A \bar{E}_A + n_A E_A^0 - n_a \bar{E}_a$$

If we now define the integral heat of adsorption as $q_{\mathrm{int}} = E_2 - E_1$, then:

$$q_{\mathrm{int}} = n_a(\bar{E}_g - \bar{E}_a) - n_A \bar{E}_e, \text{ where } \bar{E}_e = \bar{E}_A - E_A^0.$$

By definition [5], the differential heat of adsorption is:

$$q_{\mathrm{diff}} = \frac{\mathrm{d}q_{\mathrm{int}}}{\mathrm{d}n_a} \tag{9}$$

and finally:

$$q_{\mathrm{diff}} = \bar{E}_g - \bar{E}_a - \left(\frac{\partial \bar{E}_e}{\partial \Gamma}\right)_T - n_a\left(\frac{\partial \bar{E}_a}{\partial n_a}\right)_T \tag{10}$$

Relation between isosteric heat and partial molar enthalpy of adsorption

The free energy for the system aA is:

$$G_{aA} = \mu_a n_a + \mu_A n_A \tag{11}$$

and for the empty adsorbent: $G_A^0 = \mu_A^0 n_A$. Then, by definition, the excess free energy is:

$$G_e = G_{aA} - G_A^0 = \mu n_a - \Phi n_A \tag{12}$$

Thus, from $G_e = G_e(T, P, n_a, n_A)$ we obtain:

$$\mathrm{d}G_e = -S_e\,\mathrm{d}T + V_e\,\mathrm{d}P - \Phi\,\mathrm{d}n_A + \mu_a\,\mathrm{d}n_a \tag{13}$$

Consequently, using (12) and (13) and the fact that $V_e \simeq 0$ since the volume of the adsorbent does not change drastically during adsorption, we get:

$$S_e\,\mathrm{d}T - V_e\,\mathrm{d}P - n_A\,\mathrm{d}\Phi + n_a\,\mathrm{d}\mu_a = 0 \tag{14}$$

and

$$S_e\,\mathrm{d}T - n_A\,\mathrm{d}\Phi + n_a\,\mathrm{d}\mu_a = 0 \tag{15}$$

Since

$$\mathrm{d}\mu_a = \mathrm{d}\mu_g \tag{16}$$

$$S_e\,\mathrm{d}T - n_A\,\mathrm{d}\Phi + n_a RT\,\mathrm{d}\ln P + n_a R\ln P\,\mathrm{d}T = 0 \tag{17}$$

From the definitions of q_{iso} and $(-\Delta\bar{H}_{\mathrm{ads}})$, we may write:

$$q_{\mathrm{iso}} - (-\Delta\bar{H}_{\mathrm{ads}}) = RT^2\left[\left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right)_\Gamma + \left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right)_\Phi\right] \tag{18}$$

and with the help of (17) it can be shown that:

$$\begin{aligned}\left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right)_\Phi &= -\frac{S_e}{n_a}\frac{1}{\Gamma RT} - \frac{\ln P}{T}\\ \left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right)_\Gamma &= -\frac{S_e}{n_A}\frac{1}{\Gamma RT} - \frac{\ln P}{T} + \frac{1}{\Gamma RT}\left(\frac{\partial\Phi}{\partial T}\right)_\Gamma\end{aligned} \tag{19}$$

and then:

$$q_{\text{iso}}+(\Delta\overline{H}_{\text{ads}}) = \frac{T}{\Gamma}\left(\frac{\partial\Phi}{\partial T}\right)_{\Gamma} \tag{20}$$

which is the desired relation.

Relation between isosteric and differential heats of adsorption

In classical thermodynamics it is well established that:

$$\left(\frac{\partial E}{\partial V}\right)_T = t\left(\frac{\partial P}{\partial T}\right)_V - P \tag{21}$$

If we now define:

$$V_a = \frac{V}{n_a} \quad \text{and} \quad W = \frac{V}{n_A} \tag{22}$$

where V is the whole empty volume of the microporous solid adsorbent, and using the established fact in the osmotic theory of adsorption [14, 15] that:

$$\Phi = \Pi W \tag{23}$$

where Π is the osmotic pressure, we may write:

$$\left(\frac{\partial E_a}{\partial V_a}\right)_T = \left(\frac{\partial \Pi}{\partial T}\right)_{V_a} T - \Pi \tag{24}$$

With the relation $\Gamma = \frac{W}{V_a} = \frac{n_a}{n_A}$, this gives:

$$n_a\left(\frac{\partial E_a}{\partial n_a}\right)_T = \frac{\Phi}{\Gamma} - \frac{T}{\Gamma}\left(\frac{\partial\Phi}{\partial T}\right)_{\Gamma} \tag{25}$$

On the other hand, employing the thermodynamic relation:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{P,n} = -\frac{H}{T^2} \tag{26}$$

for the partial magnitudes relating to the solid adsorbent, we obtain (since the thermodynamic potential of the solid depends only weakly on pressure):

$$\left(\frac{\partial(\mu_A/T)}{\partial T}\right)_\Gamma = -\frac{H_A}{T^2} \rightarrow \left(\frac{\partial(\Phi/T)}{\partial T}\right)_\Gamma \simeq \frac{\overline{E}_e}{T^2} \tag{27}$$

for, by definition, $\Phi = -(\mu_A - \mu_A^0)$ and $\overline{H}_e = \overline{H}_A - \overline{H}_A^0 \simeq E_e = E_A - E_A^0$. Now, using the relations $H_g = E_g + RT$ and $H_a = E_a + \Pi V_a$, we may write:

$$\overline{H}_a = \overline{E}_a + \Phi/\Gamma$$

and

$$q_{\mathrm{iso}} = \overline{E}_g - \overline{E}_a + RT - \Phi/\Gamma \tag{28}$$

Finally, combining (10), (25), (27) and (28), we obtain:

$$q_{\mathrm{diff}} + T^2 \frac{\partial^2(\Phi/T)}{\partial\Gamma\partial T} = q_{\mathrm{iso}} - RT + \frac{T}{\Gamma}\left(\frac{\partial\Phi}{\partial T}\right)_\Gamma \tag{29}$$

This equation gives the desired relation between the isosteric and differential heats of adsorption.

In conclusion, it may be stated that Eq. (29) provides a possibility for a comparison between calorimetric data in terms of q_{diff} and theoretical isotherm equations in terms of q_{iso}; this emphasizes the fact in adsorption in microporous solids is necessary to take into account physical and chemical changes occurring in the solid adsorbent during adsorption.

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Zusammenfassung — Ausgehend von der Konzeption, daß der Adsorptionsprozeß in mikroporösen Festkörpern eine Auffüllung des Adsorptionsraumes und die Bildung eines monophasischen Systems (Adsorbat-Adsorbent) wie im Falle von Lösungen ist, und unter Anwendung der Thermodynamik von Lösungen wurden Ausdrücke für die isosterische Adsorptionswärme, die Adsorptionsenthalpie und die differentielle Adsorptionswärme erhalten. Nicht-triviale Beziehungen zwischen diesen thermodynamischen Größen wurden abgeleitet.

Резюме — Исходя из концепции, что адсорбционный процесс в микропористых твердых телах состоит из объемного заполнения адсорбционного пространства и образования монофазной системы (адсорбат-адсорбент), как и в случае растворов, а также используя термодинамику раствора, были получены выражения для хорошо известной изостерической теплоты адсорбции, дифференциальной теплоты адсорбции и энтальпии адсорбции. Установлены также необычные соотношения между этими термодинамическими величинами.