

## Complementary remarks to the thermodynamics of adsorption in microporous solids

### SHORT COMMUNICATION

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In a recent paper [1] some thermodynamical relations for the description of adsorption in microporous solids were established. In the present communication some complementary remarks to the former paper are made, as is stated in the title.

In the frame of thermodynamics is well established the relation:

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (1)$$

With the help of the above written relation and of the osmotic theory of adsorption [2,3]; we will obtain a relation between the differential and isosteric heats of adsorption.

Hence, if we define:

$$V_a = \frac{V}{n_a} \quad (2)$$

where  $n_a$  is the number of moles adsorbed in the adsorbent A and V is the whole empty volume of the microporous adsorbent, we could write, using [1]:

$$\left( \frac{\partial \bar{E}_a}{\partial V_a} \right)_T = T \left( \frac{\partial \Pi}{\partial T} \right)_{V_a} - \Pi \quad (3)$$

Where  $E_a$  is the partial molar energy of the adsorbate in the adsorbate-adsorbent phase and  $\Pi$  is the osmotic pressure [2,3].

Defining now:

$$W = \frac{V}{n_a} \quad (4)$$

It is obvious that, if:  $\Gamma = n_a/n_A$  where  $n_a$  is the number of moles of the adsorbate involved in the adsorption process and  $n_A$  is the number of moles of the adsorbent, then:

$$\Gamma = \frac{n_a}{n_A} = \frac{V}{V_a} \quad (5)$$

It is possible to show [1,4] that:

$$\phi = R T \int_0^P \Gamma d \ln P \quad (6)$$

in which P is the equilibrium adsorption pressure. On the other hand according to the osmotic theory of adsorption:

$$\phi = \Pi W \quad (7)$$

In this case, multiplying (3) by W it is possible to obtain:

$$\left( \frac{\partial \bar{E}_a}{\partial (1/\Gamma)} \right)_T = T \left( \frac{\partial \phi}{\partial T} \right)_\Gamma - \phi \quad (8)$$

and consequently using:  $\Gamma = \frac{n_a}{n_A}$ , it results:

$$n_a \left( \frac{\partial \bar{E}_a}{\partial n_a} \right)_T = \frac{\phi}{\Gamma} - \frac{T}{\Gamma} \left( \frac{\partial \phi}{\partial T} \right)_\Gamma \quad (9)$$

Now as it was established in [1], the differential heat of adsorption is expressed by:

$$Q_{dif} = E_g - \bar{E}_a - n_a \frac{\partial \bar{E}_a}{\partial n_a} - \left( \frac{\partial E_e}{\partial \Gamma} \right)_T \quad (10)$$

where  $E_e = \bar{E}_A - \bar{E}_A^{\circ}$  and  $\bar{E}_A, \bar{E}_A^{\circ}$  are the internal energy of the adsorbent during adsorption and fully empty of adsorbate respectively.

And the isosteric heat of adsorption is:

$$q_{iso} = \bar{H}_g - \bar{H}_a = \bar{E}_g + RT - \bar{E}_a - \Pi V_a = \bar{E}_g + RT - \bar{E}_a - \phi/\Gamma \quad (11)$$

where:

$$\bar{H}_g = \bar{E}_g + RT \quad \text{and} \quad \bar{H}_a = \bar{E}_a + \Pi V_a$$

Now combining (10) and (11)

$$q_{dif} + \left( \frac{\partial E_e}{\partial \Gamma} \right)_T = q_{iso} - RT + \frac{T}{\Gamma} \left( \frac{\partial \phi}{\partial T} \right)_\Gamma \quad (12)$$

As it is seen in (12) the term  $\left( \frac{\partial E_e}{\partial \Gamma} \right)_T$  has no explicit expression, but this relation could be obtained easily using the thermodynamical equation:

$$\left( \frac{\partial (G/T)}{\partial T} \right)_{P, \Gamma} = - \frac{H}{T^2} \quad (13)$$

for the partial molar magnitudes related with the solid adsorbent, taking into account the fact that the thermodynamical potentials for solids depends weakly on pressure:

$$\left( \frac{\partial (\mu_A/T)}{\partial T} \right)_\Gamma = - \frac{\bar{H}_A}{T^2} \quad (14)$$

Now by definition [1,4]

$$\phi = - (\mu_A - \mu_A^{\circ}) \quad (15)$$

in which  $\mu_A$  and  $\mu_A^{\circ}$  are the chemical potentials of the solid adsorbent during adsorption and empty respectively. On the other hand because of the small variation of volume of the solid during adsorption it is possible to write:

$$H_e = \bar{H}_A - \bar{H}_A^{\circ} = E_e = \bar{E}_A - E_A^{\circ} \quad (16)$$

and consequently:

$$\left( \frac{\partial (\phi/T)}{\partial T} \right)_\Gamma = \frac{E_e}{T^2} \quad (17)$$

from which it is possible to obtain:

$$\left( \frac{\partial E_e}{\partial T} \right)_{\Gamma} = T^2 \frac{\partial^2 (\phi/T)}{\partial \Gamma \partial T} \quad (18)$$

and finally:

$$q_{\text{dif}} + T^2 \frac{\partial^2 (\phi/T)}{\partial \Gamma \partial T} = q_{\text{iso}} - RT + \frac{T}{\Gamma} \left( \frac{\partial \phi}{\partial T} \right)_{\Gamma} \quad (19)$$

With this relation it is possible to make a comparison between calorimetric and adsorption isotherm measurements, testing different isotherms theoretically obtained.

Other formulation for equation (12) is (1):

$$q_{\text{dif}} = (-\Delta \bar{H}_{\text{ads}}) - RT - \left( \frac{\partial E_e}{\partial \Gamma} \right)_{\Gamma} \quad (20)$$

because:

$$q_{\text{iso}} = (-\Delta \bar{H}_{\text{ads}}) + \frac{T}{\Gamma} \left( \frac{\partial \phi}{\partial T} \right)_{\Gamma}$$

if we made  $\left( \frac{\partial E_e}{\partial \Gamma} \right)_{\Gamma} = 0$  it is seen that:

$$q_{\text{dif}} = (-\Delta \bar{H}_{\text{ads}}) - RT \quad (21)$$

which could be interpreted as if  $(-\Delta \bar{H}_{\text{ads}})$  is fundamentally related with the heat evolved as a consequence of adsorption forces as  $\left( \frac{\partial E_e}{\partial \Gamma} \right)_{\Gamma}$  is clearly related with the rearrangements occurred in the solid adsorbent during adsorption.

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Recibido: 12 de mayo de 1986.