

## Two thermodynamic approaches to the description of adsorption on solid surfaces

Alexei A. Lopatkin

Chemistry Department, Lomonosov State University, Moscow, 119899, USSR

**Abstract** - Two approaches to the thermodynamic description of adsorption on solid surfaces, viz., the method of excess functions (MEF) and the method of the layer of finite thickness (MLFT) were considered. It was shown that on the basis of corresponding fundamental equations the quantitative relations between the thermodynamic characteristics of adsorption (integral as well as differential) obtained by two methods can be deduced. Since the real distribution of adsorbate density at the solid surface is unknown, the "renormalization" of extensive thermodynamic quantities must generally take place in the MLFT.

### INTRODUCTION

At the present time there exist two main approaches to the thermodynamic description of adsorption. In this work only adsorption of one-component gas on the solid adsorbents will be considered, though the mentioned approaches are also applicable to the fluid-fluid interfaces and to the adsorption of mixtures. The first approach, which is historically due to Gibbs' initial work, will be referred to as the method of excess functions (MEF). The second approach, in which the real (physical) surface layer is considered, is called the method of the layer of finite thickness (MLFT).

For the quantitative comparison of two methods it is advisable to start with corresponding fundamental equations. In the MEF the fundamental equation can be written as follows (ref. 1):

$$dU^S = TdS^S - \phi dA + \gamma_a dm^S. \quad (1)$$

Here,  $\phi$  is analog of the "two-dimensional pressure",  $A$  is the surface area of adsorbent,  $m^S$  is the excess quantity of the adsorbed substance,  $U^S$  and  $S^S$  are the excess internal energy and excess entropy, respectively,  $\gamma_a$  is the chemical potential of adsorbate in adsorption phase. The choice of a reference system is determined by the concrete experimental procedure of measuring  $m^S$  (ref. 1). It is supposed that the surface of adsorbent,  $A$ , has a physical meaning. In some cases (e.g., the microporous adsorbents) the adsorbing surface is not present, so it is necessary, instead of the term  $dA$  to write  $dm_A$ , where  $m_A$  is the mass of adsorbent.

There exist a number of variants of the MLFT (see, e.g., ref. 2, 3). We choose the following form of the fundamental equation:

$$dU^{(\epsilon)} = TdS^{(\epsilon)} - pdV^{(\epsilon)} - \phi^{(\epsilon)}dA + \rho_a dm^{(\epsilon)} \quad (2)$$

where  $(\epsilon)$  indicates that the corresponding quantities ( $U^{(\epsilon)}$ ,  $S^{(\epsilon)}$ ,  $V^{(\epsilon)}$ , and  $m^{(\epsilon)}$ ) refer to the chosen non-homogeneous layer near the adsorbent surface. As a rule, this layer includes only adsorbate, so that the presence of solid adsorbent is taken into account only through the density changes in gas. The quantity  $V^{(\epsilon)}$  characterizes the volume of a chosen layer, and  $\tau = V^{(\epsilon)}/A$  is its thickness (the surface is supposed to be plane or nearly plane). The choice of  $V^{(\epsilon)}$  is rather arbitrary though, evidently, the values of thermodynamic quantities with index  $(\epsilon)$  depend on  $V^{(\epsilon)}$ . It is often supposed that  $V^{(\epsilon)} = \text{const.}$  and is independent of  $p$  and  $T$ . However, this supposition produces some contradictions. In the case of microporous adsorbents, as an estimation of  $V^{(\epsilon)}$  either the volume of micropores or the entire volume of solid including the pores are taken. It should be noted that if  $V^{(\epsilon)} = \text{const.}$ , the variation  $dV^{(\epsilon)}$  must be proportional to  $dA$  or to  $dm_A$ . If compared with MLFT, the MEF has the advantage of being purely phenomenological. It is in direct connection with experiment. On the contrary, the MLFT has a model character and requires some non-thermodynamic information.

#### GENERAL DEFINITIONS

As the basic quantities for the deduction of relations between the thermodynamic functions defined in MEF and MLFT, the values of adsorption  $m^s$

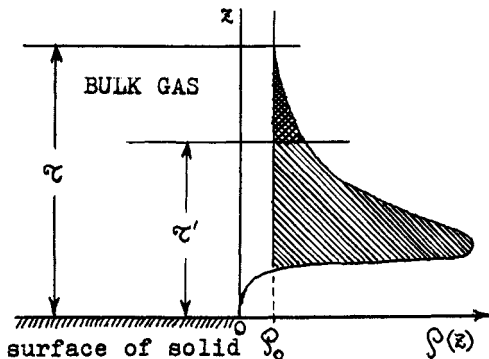


Figure. A scheme of the density distribution at the gas-solid interface

and  $m^{(\epsilon)}$  were used. To visualize the physical picture, the simplest model of adsorption of one-component gas on an ideally homogeneous plane solid surface is represented in the Figure. In this particular case, the gas molar density  $\rho$  is the function of coordinate  $z$  only. At some distance from the surface  $\rho(z) = \rho_0$ , where  $\rho_0$  is the density of bulk gas, which is in equilibrium with the adsorption phase. Let us choose the thickness of surface layer  $\tau$  so that the external boundary of the layer was situated in the region where  $\rho(z) \approx \rho_0$  (see

the Figure). Then, from the physical consideration (see, e.g., ref. 4) it is clear that

$$m^{(\epsilon)}(\tau) = m^s + \rho_0 V^{(\epsilon)}(\tau) = m^s + V^{(\epsilon)}(\tau)/\tilde{V}_g \quad (3)$$

If the bulk gas is ideal then

$$m^{(\epsilon)}(\tau) = m^s + pV^{(\epsilon)}(\tau)/RT \quad (3a)$$

Here,  $\rho_0 = 1/\tilde{V}_g$  ( $= p/RT$  for an ideal gas),  $\tilde{V}_g$  is the gas molar volume. If we introduce the average molar volume of the substance in the chosen non-homogeneous layer as  $\tilde{V}^{(\epsilon)} = V^{(\epsilon)}(\tau)/m^{(\epsilon)}(\tau) = 1/\bar{\rho}^{(\epsilon)}(\tau)$ , then the formula (3) can be rewritten in the following form:

$$m^S = m^{(\epsilon)}(\tau)(1 - \rho_0/\bar{\rho}^{(\epsilon)}(\tau)) = m^{(\epsilon)}(\tau)(1 - \tilde{V}^{(\epsilon)}(\tau)/\tilde{V}_g) \quad (3b)$$

where  $\bar{\rho}^{(\epsilon)}(\tau)$  is the average density in the volume  $V^{(\epsilon)}(\tau)$ .

It is evident that the intensive variables  $T$ ,  $p$ , and  $\gamma_a$  are identical for the two approaches because they are determined by the same equilibrium conditions (equilibrium of the gas and adsorption phases). As to the parameter

$\phi$  in eq. (1) and  $\phi^{(\epsilon)}$  in eq. (2), they are equal as well. Indeed, the relation of the Gibbs-Duhem type can be obtained by standard method from eq. (2) and thus ( $T = \text{const.}$ )

$$\begin{aligned} d\phi^{(\epsilon)} &= (m^{(\epsilon)}/A)d\gamma_a - (V^{(\epsilon)}/A)dp = (1/A)(m^{(\epsilon)}\tilde{V}_g - V^{(\epsilon)})dp = \\ &= (m^S\tilde{V}_g/A)dp = d\phi \end{aligned} \quad (4)$$

Here the eq. (3b) and the well known expression  $d\phi = (m^S RT/A)d\ln p$ , relating  $\phi$  with experimentally measured values  $m^S$  and  $p$ , were used. It follows from eq. (4) that  $\phi^{(\epsilon)} = \phi$ .

In the real cases, however, the density profile schematically represented in the Figure is unknown. When we choose, upon some considerations, the thickness of adsorption layer we do not know the actual position of external boundary of the layer. Probably, in the most cases (especially for the very widely used models of monolayer adsorption) this boundary is situated in the non-homogeneous part of layer (the layer thickness  $\tau' < \tau$ ; see the Figure). Obviously, the relation (3) is no more valid. And for the quantity  $m^{(\epsilon)}(\tau')$  we obtain

$$m^{(\epsilon)}(\tau') = m^S + \rho_0 V - A \int_{z(\tau')}^{z_{\max}} \rho(z) dz \quad (5)$$

where  $V$  is the volume of the entire system, excluding the proper volume of adsorbent,  $z(\tau')$  is the coordinate  $z$  for the layer boundary determined by  $\tau'$ ,  $z_{\max}$  is the coordinate of the upper boundary of (cylindrical) adsorption vessel. The third term on the right-hand side of (5) cannot be determined from experiment. That is why on the recalculation of measured excess adsorption  $m^S$  into the full content of the substance one obtain not a  $m^{(\epsilon)}(\tau)$  value but some other quantity,  $\hat{m}^{(\epsilon)}(\tau')$ , defined by the following relation analogous to (3):

$$\hat{m}^{(\epsilon)}(\tau') = m^S + \rho_0 V^{(\epsilon)}(\tau') = m^{(\epsilon)}(\tau') + A \int_{z(\tau')}^{z_{\max}} (\rho(z) - \rho_0) dz \quad (6)$$

So, some "renormalization" ("redefinition") of adsorption is the case in the MLFT. The integral in (6) is proportional to the area in the Figure with criss-cross shading (and the entire shaded area is proportional to  $m^S$ ). The quantity  $\hat{m}^{(\epsilon)}(\tau')$  can be calculated by formula (6) from experimental data but in general its physical significance is not that of the adsorbate quantity in some surface layer. The analogous "renormalization" must be carried out for all other extensive quantities in eq. (2). As a result of this procedure, they also may lose their physical meaning. It can be shown that the quantity  $\hat{\rho}^{(\epsilon)}$  involved in the correspondingly transformed eq. (2)

is equal to  $\phi$ . The real "two-dimensional" pressure for the layer of thickness  $\tau'$  is obviously not equal to  $\phi$ , as it follows from the "mechanical" definition of  $\phi$  (ref. 3).

It is to be emphasized that the relations written below have the same form irrespective of using, as basic, the quantity  $m^{(\epsilon)}(\tau)$  or  $\hat{m}^{(\epsilon)}(\tau')$ , because the equations (3) and (6) are formally identical. Therefore we omit specifications ( $\tau$ ) and ( $\tau'$ ) bearing in mind that in the second case the extensive quantities do not have the physical meaning that they have in the first case.

#### INTERDEPENDENCE OF MEF AND MLFT THERMODYNAMIC FUNCTIONS

We shall find firstly the connection between the integral functions, viz., entropies  $S^s = S^s/m^s$  and  $S^{(\epsilon)} = S^{(\epsilon)}/m^{(\epsilon)}$ . From the fundamental equations (1) and (2) and the equilibrium conditions it follows (see, e.g., ref. 1)

$$\begin{aligned} \tilde{Z}RT(\partial \ln p / \partial T)\phi &= (\tilde{S}_g - \tilde{S}^{(\epsilon)}) / (1 - (\tilde{v}^{(\epsilon)} / \tilde{v}_g)) - (m^{(\epsilon)} / m^s) (\tilde{S}_g - \tilde{S}^{(\epsilon)}) = \\ &= \tilde{S}_g - \tilde{S}^s \end{aligned} \quad (7)$$

where  $\tilde{Z} = p\tilde{v}_g/RT$  is the compressibility factor for a real gas. From eq. (7) we obtain

$$\tilde{S}^{(\epsilon)} = \tilde{S}^s (m^s / m^{(\epsilon)}) + \tilde{S}_g (\tilde{v}^{(\epsilon)} / \tilde{v}_g) = \tilde{S}^s + (\tilde{S}_g - \tilde{S}^s) (\tilde{v}^{(\epsilon)} / \tilde{v}_g) \quad (8)$$

where  $\tilde{S}^s$  is the primary quantity that can be determined from experimental data, and  $\tilde{S}^{(\epsilon)}$  is obtained by recasting with use of eq. (8). It can be seen from (8) that  $\tilde{S}^{(\epsilon)} > \tilde{S}^s$ . In all cases when it is possible to assume that  $\tilde{v}^{(\epsilon)} \ll \tilde{v}_g$ ,  $\tilde{S}^{(\epsilon)} \approx \tilde{S}^s$ . However, in the region of very high equilibrium pressures the analysis of eq. (8) meets some difficulties. As it can be shown (see, e.g., ref. 1),

$$\begin{aligned} T(\tilde{S}_g - \tilde{S}^s) &= T(m^{(\epsilon)} / m^s) (\tilde{S}_g - \tilde{S}^{(\epsilon)}) = \tilde{H}_g - \tilde{U}^s - (\phi / \Gamma) = \\ &= (m^{(\epsilon)} / m^s) (\tilde{H}_g - \tilde{U}^{(\epsilon)}) - p\tilde{v}^{(\epsilon)} - (\phi / \Gamma^{(\epsilon)}) \end{aligned} \quad (9)$$

And we obtain from (9) the following relation between  $\tilde{U}^{(\epsilon)}$  and  $\tilde{U}^s$ , similar to eq. (8):

$$\tilde{U}^{(\epsilon)} = \tilde{U}^s (m^s / m^{(\epsilon)}) + \tilde{U}_g (\tilde{v}^{(\epsilon)} / \tilde{v}_g) \quad (10)$$

In eq. (9)  $\Gamma = m^s/A$  and  $\Gamma^{(\epsilon)} = m^{(\epsilon)}/A$ .

When we pass to the differential quantities, the situation becomes more complicated and it is necessary to precise the model of the layer of finite thickness. As an example of the general approach, we shall obtain now the relation between the isosteric heats of adsorption,  $q_{st}$  and  $q_{st}^{(\epsilon)}$ , using as in the previous case the equations (1) and (2) and the equilibrium conditions. In the MEF

$$q_{st} = \tilde{Z}RT^2(\partial \ln p / \partial T)_\Gamma \quad (11)$$

and in the MLFS

$$q_{st}^{(\epsilon)} = \tilde{Z}RT^2(1 - (\tilde{v}_a^{(\epsilon)} / \tilde{v}_g))(\partial \ln p / \partial T)_{\Gamma^{(\epsilon)}} \quad (12)$$

The widely adopted condition  $\bar{V}^{(\sigma)} = \text{const.}$  (see above) leads to the conclusion that the differential (or partial molar) volume  $\bar{V}_a^{(\sigma)}$ , defined by relations

$$\bar{V}_a^{(\sigma)} = (\partial y_a / \partial p)_{T, \Gamma^{(\sigma)}} = (\partial V^{(\sigma)} / \partial m^{(\sigma)})_{p, T, m_A} \quad (I3)$$

is equal to zero, as well as to some other not justified consequences. In principle, not complicated but rather tiresome deduction gives the following general relation:

$$q_{st}^{(\sigma)} = (1 - (\bar{V}_a^{(\sigma)} / \bar{V}_g)) q_{st} (1 + (T/q_{st})(\partial p / \partial m^S)_T (V^{(\sigma)} (\partial \ln \bar{V}_g / \partial T)_p - (\partial V^{(\sigma)} / \partial T)_p)) / (1 - (1/\bar{V}_g)(\partial p / \partial m^S)_T (V^{(\sigma)} (\partial \ln V_g / \partial p)_T - (\partial V^{(\sigma)} / \partial p)_T)) \quad (I4)$$

In this formula the nonideality of gas and the possible changes in adsorbent under the influence of temperature and pressure are taken into account. If we neglect the dependence of  $V^{(\sigma)}$  on  $p$  and  $T$  and suppose the bulk gas to be ideal, the eq. (I4) can be essentially simplified. On analysing (I4), some difficulties arise, especially in the region of pressures where the isotherm of excess adsorption  $m^S$  passes through a maximum. Here, the "excess" isosteric heat  $q_{st}$  is the primary quantity that can be determined directly from experimental data.

Since  $q_{st} = T(\tilde{S}_g - \bar{S}^S) = (\tilde{H}_g - \bar{U}^S)$  and  $q_{st}^{(\sigma)} = T(\tilde{S}_g - \bar{S}^{(\sigma)}) = (\tilde{H}_g - \bar{U}^{(\sigma)} - pV_a^{(\sigma)})$ , where  $\bar{S}^S = (\partial S^S / \partial m^S)$ ;  $\bar{S}^{(\sigma)} = (\partial S^{(\sigma)} / \partial m^{(\sigma)})$ ;  $\bar{U}^S = (\partial U^S / \partial m^S)$ , and  $\bar{U}^{(\sigma)} = (\partial U^{(\sigma)} / \partial m^{(\sigma)})$ , it is possible to obtain from (I4) the general relations between  $\bar{S}^S$  and  $\bar{S}^{(\sigma)}$ , and between  $\bar{U}^S$  and  $\bar{U}^{(\sigma)}$ , which are not given here because of its cumbersome appearance.

## CONCLUSION

It is necessary to underline that the measured quantity  $m^S$  has in general case not completely clear physical significance, since the number of factors, such as the changes of adsorbent under the action of adsorbed substance, pressure and temperature; adsorption of the calibration gas; molecular sieve effect etc. , is not (and cannot be) taken into account. This consideration concerns evidently the quantity  $m^{(\sigma)}$ , which one calculates using  $m^S$ , and other thermodynamic characteristics of adsorption layer as well.

Finally, it should be pointed out that the MLPT can be easily translated into the language of excess functions if we properly choose a fully artificial reference system, which has no connection with experiment at all.

## REFERENCES

1. A.A. Lopatkin, Theoretical Foundations of Physical Adsorption, Moscow University Press, Moscow (1983) (in Russian).
2. T.L.Hill, in Advances in Catalysis, **4**, 211-255 (1952).
3. W.A.Steele, The Interaction of Gases with Solid Surfaces, Pergamon Press, Oxford (1974).
4. R.J.Tykodi, J. Chem. Phys. **22**, N#10, 1647-1654 (1954).