Negative Gas−Solid Adsorption and Its Influence on Wettability[1]

Malcolm E. Schrader†

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

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For the past 60 years it has been widely accepted among surface chemists involved with contact angle and wettability that exposure of an evacuated solid surface to any vapor will reduce the free energy of that solid surface. We show that this is a misconception which arises from the use of absolute adsorption in the free energy equation. When the adsorption is formulated as a "surface-excess" it is apparent that the free energy change on adsorption can be positive or negative, depending on whether the adsorption is negative or positive. We point out that evidence of the existence of negative adsorption in gas−solid interaction has been accumulating. Specifically we show that exposure of an evacuated Teflon (PTFE) surface to water vapor may result in negative adsorption which, of course, indicates that it has undergone an *increase* in surface free energy.

Introduction

There has been a widely accepted view for the past 60 years that the exposure of any evacuated solid surface to the vapor of a liquid must decrease the free energy of that solid surface. It was accordingly assumed that this would decrease the tendency of the solid to spread that liquid, thereby increasing the equilibrium contact angle. In this paper we discuss whether there really is a thermodynamic requirement that vapor adsorbed to an evacuated surface must lower the free energy of that surface.

Gibbs Adsorption Isotherm

Bangham and Razouk[2,3] first applied the Gibbs "adsorption isotherm" to gas−solid systems. This adaptation was accomplished by using the Guggenheim−Adam[4] modification of the Gibbs isotherm[5] which allows the Gibbs boundary to be fixed at the exact surface of the solid. For a vapor−solid system they then write

$$-\mathrm{d}\,\gamma = RT\,\Gamma\,\mathrm{d}\ln p \qquad (1)$$

which gives the relationship between the decrease in free energy γ at the solid−gas interface, the increase in pressure p, and the gas "adsorption" Γ at that interface. The total free energy change on adsorbing vapor to the evacuated surface at pressure p is then obtained by integrating eq 1 to obtain

$$-\Delta F = \Pi_e = RT\int_0^{p^\circ}\Gamma\,\mathrm{d}\ln p \qquad (2)$$

where ΔF is the free energy change occurring from adsorption of vapor from $p = 0$ to the designated pressure, taken here as p°, the saturation pressure. The quantity Π is defined as $-\Delta F$, written as Π_e when the adsorption is at the saturation pressure p°.

We note that the derivation of eq 2 uses a variation of the Gibbs relationship which, in any form, concerns the mutual dependency of surface free energy, pressure (or its equivalent), and "adsorption" defined as surface-excess per unit area. In his first[2] publication on the subject of Π_e Bangham specifically implies that adsorption, as he uses it, is a surface-excess. In his second[3] and third,[6] he does not call attention to it at all. Thus, starting with Bangham and Razouk themselves, use of eq 2 in the field of wettability has always dealt with "positive" adsorption, which came to be regarded as absolute adsorption. Barring electrostatic effects, absolute adsorption must always be positive since there are always attractive forces. Furthermore, by definition it cannot be less than zero. We shall show below, however, that an absolute positive adsorption calculated for a vapor−solid system of interest to wettability can actually be a negative surface excess. We shall show that this is reasonable in terms of surface thermodynamics. Furthermore, it will be shown that in the field of critical phenomena, negative gas−solid adsorption is now widely predicted from statistical−mechanical calculations.

Water on Polyethylene and Teflon (PTFE)

The absolute adsorption of water on polyethylene and PTFE, respectively, has been estimated by calculation based on the "nearest neighbor" approximation.[7] For polyethylene, the fraction of the surface covered was given as 7×10^{-6}. For PTFE the value calculated was 6×10^{-7} mol fraction of surface sites covered. In the following we convert "mole fraction ...covered" to surface-excess.

The adsorption volume for H_2O on a square centimeter of surface may be estimated as that of a cylinder of cross-section 1 cm^2 and height of 0.311 nm, the latter the approximate diameter of a water molecule. For water vapor at 20 torr there are 3.65×10^{-14} mol in a volume of this size in the bulk phase, which may be taken as zero surface-excess for adsorption. Assuming that there are 1.034×10^{15} sites per square centimeter available for H_2O adsorption, the absolute values for adsorption are 1.202×10^{-14} mol/cm^2 for polyethylene and 1.031×10^{-15} mol/cm^2 for PTFE. The surface excesses calculated are given in the last column of Table 1. It can be seen that negative surface excesses are predicted for gas−solid adsorption, at p°, on both polyethylene and PTFE.

Now, it can be seen from eq 1 that if the surface excess is positive, then an increase in the pressure of a vapor will result

† Telephone: 972-2-6585617. Fax: 972-2-6585319. E-mail: schrader@vms.huji.ac.il.

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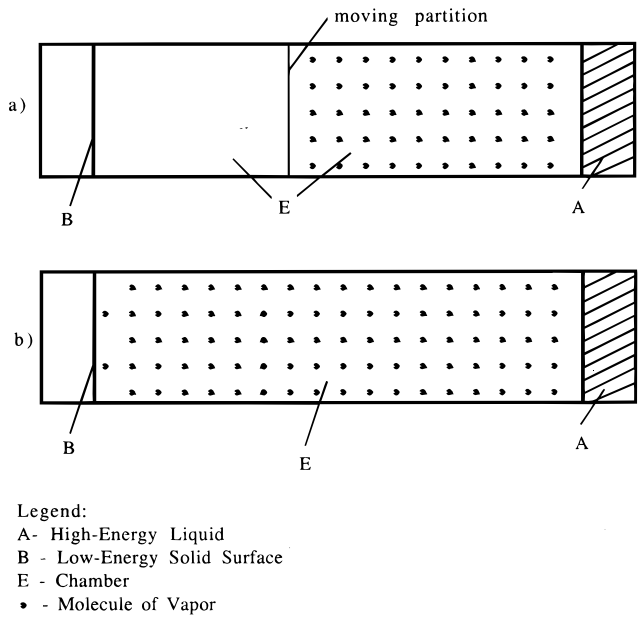

Figure 1. Vapor–solid adsorption. (a) Liquid vapor at $p°$ evaporating and gradually filling up space. (b) Space filled at $p°$; deficiency of molecules near low-energy solid.

TABLE 1: Surface Excesses Calculated for Adsorption of Water on Polyethylene and PTFE

solid	fraction of sites covered[7]	absolute adsorption (mol/cm^2)	surface excess (mol/cm^2)
polyethylene	7×10^{-6}	1.202×10^{-14}	-2.46×10^{-14}
Teflon (TFE)	6×10^{-7}	1.031×10^{-15}	-3.55×10^{-14}

in a decrease in free energy of the solid–vapor interface. However, if the surface excess of a vapor is negative, as is calculated for water vapor on polyethylene or PTFE, then an increase in pressure of the vapor will result in an *increase* in free energy of the solid–vapor interface. It is also correct to state that the *absolute* adsorption, which takes place, of water vapor to polyethylene or Teflon, at $p°$, results in an *increase* in free energy of the solid–vapor interface.

Thermodynamics of Negative Adsorption in Vapor-Solid Systems

It is of interest, at the same time, to examine the specific thermodynamic interactions involved in the liquid–vapor–solid system to obtain a qualitative explanation of the negative adsorption. It is convenient to work from the model of Figure 1. The vapor is confined to the enclosure E, where, for convenience, the nature of the walls are ignored except for the areas A and B. Area A is covered by a flat film of the liquid in equilibrium with its vapor in the enclosure E, at pressure $p°$. There is no change in free energy on condensation or evaporation of the liquid. We allow the vapor to slowly and reversibly fill the space at $p°$ by slowly moving the partition C in the direction from wall A to wall B. On reaching the low-energy wall B the partition is removed.

During the space-filling process we have

$$\Delta F = \Delta H - T\Delta S = 0 \tag{3}$$

where F is the Gibbs free energy, H is the enthalpy, T the temperature, and S the entropy, so that

$$\Delta H = T\Delta S \tag{4}$$

The meaning here is that evaporation from the surface A to the space of E requires an energy ΔH per mol to transfer the molecules from liquid to vapor phase. At the same time, the molecules gain in entropy from release from the liquid to the gas phase, so that the required ΔH input is balanced by the $T\Delta S$ term which drives the expansion. When the vapor reaches the area B, $T\Delta S$ will suddenly decrease due to the presence of the surface, thus removing much of the previous driving force of the evaporation.

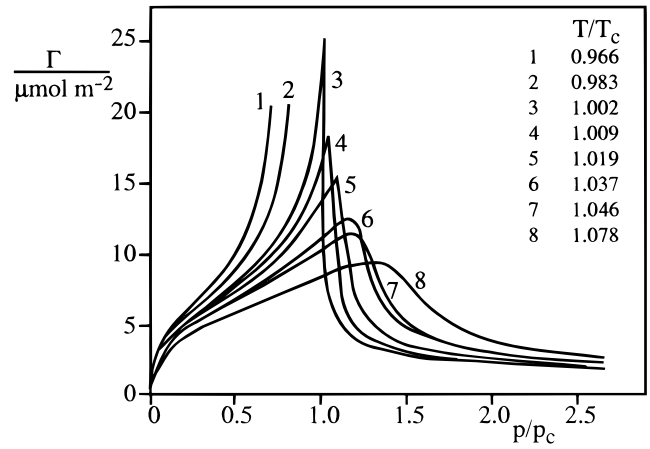

Figure 2. High-temperature adsorption isotherms of SF_6 graphitized carbon black; the experimental excess-surface concentration is plotted as a function of the reduced pressure. Reprinted with kind permission of Kluwer Academic Publishers from G. H. Findenegg in *Theoretical Advancement in Chromatography and Related Separation Techiques*; F. Dondi and G. Guiocion, Eds., 1992; p. 233, Figure 3.

In general there are possibilities for formation of a liquid film on a surface in the position of B in such a situation. In order for this to happen, however, the H evolved as a result of adsorption at that surface would have to be equal to or greater than the H required to evaporate the molecules from the liquid film at A. A full adlayer would then build up which would adsorb molecules to itself and ultimately build up a bulk liquid film. The surface B however, is a low-energy surface. ΔH of adsorption will then be much less than ΔH of evaporation of a molecule, say water, from the high-energy liquid. Therefore, the enthalpy change (which now approximates the free energy change since the entropy term more or less cancels out) to remove molecules from the bulk liquid in film A to supply them to interface B will not be available. That is, the enthalpy given off during adsorption at B is not sufficient to evaporate a molecule from the liquid at A. There will consequently be a deficiency of molecules at interface B.

Other Indications of Negative Adsorption

A considerable body of evidence, including experiments as well as statistical mechanical calculations, is available in support of the concept of negative adsorption of gases to solids above the critical temperature or even below it for certain values of the energy constants. Adsorption isotherms are generally reported in terms of the total amount adsorbed from the beginning of the experiment. Thus, it is possible that as successive increments of gas are adsorbed, at first each increment results in some adsorption taking place (as surface excess). Subsequently however, a given increment may yield negative adsorption. This combination will manifest itself, when continued, as a maximum in the adsorption curve. Thus, while all values of Γ throughout the course of the experiment may remain in the positive region, incremental adsorption is actually

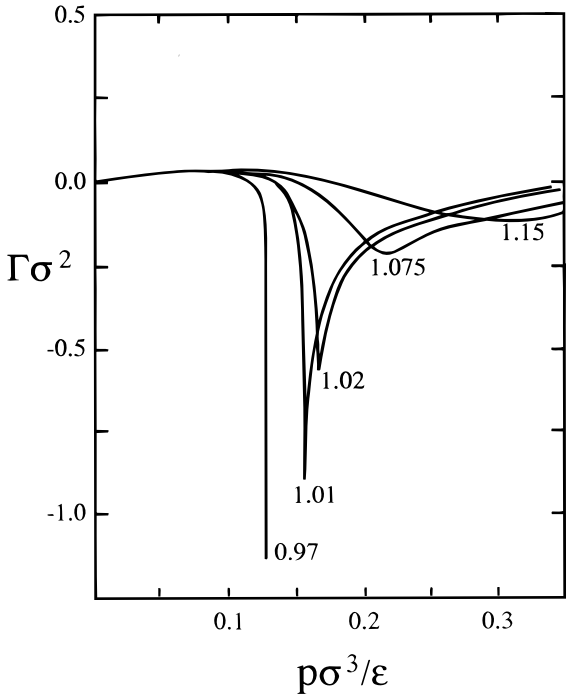

Figure 3. Adsorption isotherms for weakly adsorbed gases. Reprinted with permission of the American Chemical Society from Figure 5 of Henderson, D.; Snook, I. K. *J. Phys. Chem.* **1983**, *87*, 2956.

negative after Γ passes through the maximum. According to Henderson,[8] the equation predicting possible negative adsorption in gas solid systems was first derived by Steele,[9] then by others.[10−12]

An example of this result may be seen in the experimentally determined adsorption of sulfur hexafluoride onto graphitized carbon black[13] in Figure 2. This behavior is attributed to surface-excess isotherms in general and explained by Findenegg[13,14] as due to "repulsive interactions between the molecules in the boundary layer become appreciable and will outweigh the attractive gas−surface interaction". Henderson and Snook[8] use the term negative adsorption in reporting their results, which include one striking case where Γ (the total amount adsorbed) remains negative throughout nearly the entire isotherm (Figure 3). They state "For weakly adsorbed gases, the MSA (mean spherical approximation) predicts negative values for the adsorption including negative extrema in the critical region. Such isotherms have not been observed experimentally but might be seen in carefully chosen systems."

Adsorption maxima in the critical region for gases on solid surfaces have often been predicted from statistical mechanical calculations, including those by Sokolowski,[15] Henderson,[8] Badiali[16] et al., del Rio,[17] and Donohue.[18] They have been observed experimentally by Specovius and Findenegg[19] and in computer simulations of van Megen and Snook.[20]

Conclusions

1. Gas−solid adsorption measurements yield surface-excess isotherms.
2. These display positive or negative adsorption.
3. The free energy of an evacuated solid surface may thus decrease or increase on adsorption of vapor (positive or negative Π respectively).
4. If that free energy change indeed affects the contact angle, it will increase or decrease it, accordingly.

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