THE THEORY OF ADSORPTION AND CATALYSIS

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PREFACE

One of the main functions of science is to develop theories that explain and predict. In adsorption and catalysis, explanations are still tentative and predictions precarious, for surface phenomena are unusually difficult to observe and measure. So, unavoidably, the following pages are full of fledgling theories, some of which may never pass the test of sustained flight. However, such theories are worth reviewing because they help to polarize thinking and to pose sharp questions.

A quantitative and nonempirical approach has been adopted so far as possible. Although empirical equations often can be made to fit experimental data better, they explain less about mechanisms. The approach works best for physical adsorption, where surprisingly simple models frequently turn out to be useful caricatures of reality. The treatment grows increasingly qualitative and empirical, for it becomes increasingly difficult to devise suitable models as the complexity mounts from physical adsorption to chemisorption to catalysis. Tacitly indicated is the enormous amount of research, theoretical and experimental, yet to be done.

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PART

I

ADSORPTION

CHAPTER

I

THERMODYNAMICS OF ADSORPTION

1.1 Introduction

Solid catalysts work by adsorbing at least one reactant. Therefore, a knowledge of adsorption is necessary for a fundamental understanding of catalysis.

Adsorption on solid surfaces is a complex phenomenon. Most catalytic surfaces are not uniform. They consist of sites with a broad distribution of adsorption energies and irregular surface patterns. The density of sites may be extremely low or so high as to form a continuum. The adsorbed molecules may be mobile or immobile. They may be independent of each other or they may interact with their nearest neighbors or even with more distant ones, and, as a result, undergo phase transformations. The forces binding foreign molecules to a surface may be physical, including van der Waals' attraction forces and the forces developed by dipoles and ions as they approach surfaces; or they may be equivalent to the forces in chemical bonds involving molecular orbital overlap. In theory, physical adsorption and chemical adsorption are easily distinguishable, but no experimental criteria are available yet to make completely reliable distinctions in practice. Perturbations of surface atoms or ions may occur as a result of adsorption. It is usually assumed that perturbations intensify with increasing strength of the adsorption bond. Since the forces of physical adsorption are often much weaker than chemical forces, the assumption is frequently made that perturbations can be neglected in the case of physical adsorption. In any event, no satisfactory methods are available for dealing with these perturbations.

Obviously, specific models must be used in the attempt to bring order into the complexity of the adsorption picture. We propose to treat adsorption models in the order of their increasing specificity. The classical thermodynamic approach of this chapter introduces the least physical restrictions into the treatment of adsorption phenomena. The relationships developed are more generally true than those of subsequent chapters. But the price we pay for not being more specific in our model is the loss of detailed information about the adsorption process. When, as in subsequent chapters, we specify that the adsorbed molecules are mobile (or immobile), our model loses generality, but gains much in detailed information about those real systems for which it is an approximation. Even more detailed information accrues from models in which the nature of the adsorption forces are stipulated.

We shall now derive the most important results of the application of classical thermodynamics to surfaces. We shall assume that the adsorbent is unperturbed, that it may be considered as an inert material supplying a potential field for the adsorbate. First the differential energy equation will be derived in the form applicable to adsorption, and from it the other thermodynamic functions. Next, these functions will be used to derive expressions for four important isothermal heats of adsorption: the isosteric heat, the differential heat, the equilibrium heat, and the equilibrium energy of adsorption. The relationships between these heats will then be derived. Finally, we shall develop an expression for the adiabatic heat of adsorption. A knowledge of elementary classical thermodynamics is assumed.

1.2 Fundamental Equations

In ordinary three-dimensional thermodynamics, the total energy E is a function of three independent variables which are most conveniently selected to be S, the total entropy; V, the total volume; and n_i, the number of moles of each species present in the system. The differential energy is written

$$dE = T\,dS - P\,dV + \sum \mu_i\,dn_i, \tag{1}$$

which may be integrated holding intensive variables temperature T, pressure P, and chemical potentials μ_i, constant to give

$$E = TS - PV + \sum \mu_i n_i. \tag{2}$$

In two-dimensional, or adsorption thermodynamics, we will show that an additional work term is required. Following Hill (*1–3*), we start from the thermodynamics of solutions and, with appropriate assumptions, arrive at equations applicable to adsorption. Consider a two-component condensed phase containing n_A moles of a nonvolatile component and n_s moles of a volatile component in equilibrium with the gas phase. The differential energy of the *condensed* phase is

$$dE = T\,dS - P\,dV + \mu_A\,dn_A + \mu_s\,dn_s, \tag{3}$$

where P is the *hydrostatic* pressure exerted by a hypothetical piston or (in part) by a hypothetical inert additional gas on the volume of the condensed phase.

The equation applies to such diverse systems as argon–graphite, hydrogen–tungsten, hydrogen–charcoal, hydrogen–palladium, benzene–rubber, water–sodium chloride, and water–sulfuric acid. If the nonvolatile component is a solid, it is understood that a change dn_A in n_A refers to solid of the same state of subdivision, specific surface, etc. For the pure substance, we write

$$dE_{0A} = T\,dS_{0A} - P\,dV_{0A} + \mu_{0A}\,dn_A. \tag{4}$$

The following quantities are now defined:

$$E_s \equiv E - E_{0A}, \qquad V_s \equiv V - V_{0A}, \qquad S_s \equiv S - S_{0A}, \qquad \Phi \equiv \mu_{0A} - \mu_A. \tag{5}$$

So far these quantities have no special significance physically. For example, E_s is just the difference between the total energy of the condensed phase and the energy of n_A moles of pure substance. By subtracting Eq. (4) from Eq. (3), we obtain the differential energy

$$dE_s = T\,dS_s - P\,dV_s - \Phi\,dn_A + \mu_s\,dn_s. \tag{6}$$

In order to make the transition to adsorption thermodynamics, we stipulate that the n_A moles of nonvolatile substance are inert. For this special case, E_s, for example, becomes just the energy of n_s moles of adsorbed molecules in the potential field of the surface of the inert adsorbent (the energy of the adsorbent subtracts out except for the interaction energy between adsorbent and adsorbed molecules, which is left in E_s). Similar meanings apply to V_s and S_s. In the identity $\Phi \equiv \mu_{0A} - \mu_A$, μ_{0A} is the chemical potential of pure adsorbent with clean surface and μ_A is the chemical potential of pure adsorbent with a surface layer of adsorbate. We have

$$\begin{aligned} (\partial E_{0A}/\partial n_A)_{S_{0A}, V_{0A}} &= \mu_{0A}, \\ (\partial E/\partial n_A)_{S, V, n_s} &= \mu_A, \\ \Phi \equiv \mu_{0A} - \mu_A &= -(\partial E_s/\partial n_A)_{S_s, V_s, n_s}. \end{aligned} \tag{7}$$

Thus, the difference $\Phi \equiv \mu_{0A} - \mu_A$ represents the energy change per unit of adsorbent in the surface spreading of adsorbate. We assume that, for an inert adsorbent, n_A is proportional to surface area α, so that

$$\Phi \, dn_A = \Phi c \, d\alpha \equiv \varphi \, d\alpha, \tag{8}$$

and

$$\varphi = -(\partial E_s/\partial \alpha)_{S_s, V_s, n_s}. \tag{9}$$

The quantity $\varphi \, d\alpha$ is the two-dimensional equivalent of the three-dimensional work term $P\,dV$, and φ is often called the "spreading pressure." It is well known that $\varphi = \gamma_0 - \gamma$, where γ_0 is the surface tension of the clean surface and γ is the surface tension of the surface with adsorbate.

We may now write

$$dE_s = T\,dS_s - P\,dV_s - \varphi \, d\alpha + \mu_s \, dn_s \tag{10}$$

for the energy differential of a one-component system of n_s moles of adsorbed gas.

So long as the adsorbent is truly inert, Eq. (10) is useful. From here on we shall assume an inert adsorbent. Whether or not this is a completely valid assumption is a difficult question. For weak adsorption, the assumption is usually considered justifiable, but not for strong adsorption. The question will be discussed further in Chapter VI.

The fundamental equations of adsorption thermodynamics can now be set up, based on the approximation of an inert adsorbent and a one-component system of n_s moles of adsorbed gas. A complete set of thermodynamic functions will be provided from which the various heats of adsorption may then be conveniently derived (see Section 1.3). We use Eq. (10) and the following definitions of enthalpy H_s, Gibbs free energy F_s, and the Helmholtz free energy A_s:

$$\begin{aligned} H_s &\equiv E_s + PV_s, \\ F_s &\equiv H_s - TS_s, \\ A_s &\equiv E_s - TS_s. \end{aligned} \tag{11}$$

From these, the following fundamental equations for thermodynamic differentials are obtained:

$$dE_s = T\,dS_s - P\,dV_s - \varphi \, d\alpha + \mu_s \, dn_s, \tag{12}$$

$$dH_s = T\,dS_s + V_s\,dP - \varphi \, d\alpha + \mu_s \, dn_s, \tag{13}$$

$$dA_s = -S_s\,dT - P\,dV_s - \varphi \, d\alpha + \mu_s \, dn_s, \tag{14}$$

$$dF_s = -S_s\,dT + V_s\,dP - \varphi \, d\alpha + \mu_s \, dn_s. \tag{15}$$

By integrating with all intensive variables constant:

$$E_s = E_s(S_s, V_s, \alpha, n_s) = TS_s - PV_s - \varphi\alpha + \mu_s n_s, \tag{16}$$

$$H_s = H_s(S_s, P, \alpha, n_s) = TS_s - \varphi\alpha + \mu_s n_s, \tag{17}$$

$$A_s = A_s(T, V_s, \alpha, n_s) = -PV_s - \varphi\alpha + \mu_s n_s, \tag{18}$$

$$F_s = F_s(T, P, \alpha, n_s) = -\varphi\alpha + \mu_s n_s. \tag{19}$$

In these equations, we see that four independent variables are required to describe completely each thermodynamic variable, whereas in ordinary three-dimensional thermodynamics, only three variables are needed for a one-component system. In each equation, the area α is taken as an independent variable.

From the fundamental equations, φ and μ_s are defined by

$$\begin{aligned}\varphi \equiv -(\partial E_s/\partial\alpha)_{S_s, V_s, n_s} &= -(\partial H_s/\partial\alpha)_{S_s, P, n_s} \\ &= -(\partial A_s/\partial\alpha)_{T, V_s, n_s} = -(\partial F_s/\partial\alpha)_{T, P, n_s},\end{aligned} \tag{20}$$

$$\begin{aligned}\mu_s \equiv (\partial E_s/\partial n_s)_{S_s, V_s, \alpha} &= (\partial H_s/\partial n_s)_{S_s, P, \alpha} \\ &= (\partial A_s/\partial n_s)_{T, V_s, \alpha} = (\partial F_s/\partial n_s)_{T, P, \alpha}.\end{aligned} \tag{21}$$

1.3 Isothermal Heats of Adsorption

First, we shall derive expressions for two *differential* heats of adsorption, making use of the thermodynamic differentials, Eqs. (14) and (15). Then we shall derive expressions for two *integral* heats of adsorption from the integrated thermodynamic formulas, Eqs. (18) and (19). The definitions of these four isothermal heats of adsorption follow from their derivations. We begin by deriving an expression for the differential heat known as the isosteric heat of adsorption, q_{st}, using Eq. (15) in conjunction with the equation

$$\begin{aligned}d\mu_s = (\partial\mu_s/\partial T)_{P, ns, \alpha}\, dT + (\partial\mu_s/\partial P)_{T, n_s, \alpha}\, dP \\ + (\partial\mu_s/\partial n_s)_{T, P, \alpha}\, dn_s + (\partial\mu_s/\partial\alpha)_{T, P, n_s}\, d\alpha.\end{aligned} \tag{22}$$

Substituting in this equation, $(\partial F_s/\partial n_s)_{T, P, \alpha} = \mu_s$, and noting that

$$\begin{aligned}\left[\frac{\partial(\partial F_s/\partial n_s)_{T, P, \alpha}}{\partial T}\right]_{P, n_s, \alpha} &= \left[\frac{\partial(\partial F_s/\partial T)_{P, ns, \alpha}}{\partial n_s}\right]_{T, P, \alpha} \\ &= -(\partial S_s/\partial n_s)_{T, P, \alpha} \equiv -\bar{s}_s,\end{aligned} \tag{23}$$

and similarly that

$$(\partial\mu_s/\partial P)_{T, n_s, \alpha} = (\partial V_s/\partial n_s)_{T, P, \alpha} \equiv \bar{v}_s, \tag{24}$$

$$(\partial\mu_s/\partial\alpha)_{T, P, n_s} = -(\partial\varphi/\partial n_s)_{T, P, \alpha}, \tag{25}$$

we obtain

$$d\mu_s = -\bar{s}_s\, dT + \bar{v}_s\, dP - (\partial\varphi/\partial n_s)_{T,P,\alpha}\, d\alpha + (\partial\mu_s/\partial n_s)_{T,P,\alpha}\, dn_s. \qquad (26)$$

A change in μ_s at constant amount adsorbed ($dn_s = 0$) and at constant adsorbent area ($d\alpha = 0$) gives

$$d\mu_s = -\bar{s}_s\, dT + \bar{v}_s\, dP. \qquad (27)$$

At equilibrium with the gas $d\mu_s = d\mu_G$, or

$$-\bar{s}_s\, dT + \bar{v}_s\, dP = -s_G\, dT + v_G\, dp, \qquad (28)$$

where

$$s_G \equiv S_G/n_G = (\partial S_G/\partial n_G)_{T,p}, \qquad v_G \equiv V_G/n_G = (\partial V_G/\partial n_G)_{T,p},$$

and p is the equilibrium gas pressure. Note that $\bar{s}_s$ and $\bar{v}_s$ are differential molar quantities at constant temperature, pressure and surface area, and in general vary with n_s in contrast to s_G and v_G which are integral molar quantities and independent of n_G at constant T and p. We shall always express a molar quantity by a lower-case letter, and shall place a bar above it for the differential molar quantity at constant T, p, and α, for example,

$$(\partial F_G/\partial n_G)_{T,p} = \mu_G = F_G/n_G \equiv f_G;$$

$$(\partial F_s/\partial n_s)_{T,p,\alpha} = \mu_s = (\partial f_s/\partial n_s)_{T,p,\alpha} n_s + f_s \equiv (\partial f_s/\partial n_s)_{T,p,\alpha} n_s + F_s/n_s) \equiv \bar{f}_s.$$

Thus $\bar{f}_s = f_s$ only if $(\partial f_s/\partial n_s)_{T,p,\alpha} = 0$, which is not true in general.

Under usual conditions, the hydrostatic pressure P on the adsorbed layer consists only of the equilibrium gas pressure p and therefore $P = p$. Alternatively the hydrostatic pressure P may be assumed constant ($dP = 0$) while p changes with temperature. However, variations in P have little effect on the adsorbed volume V_s which is small in comparison to V_G and virtually incompressible. Thus

$$(\partial \ln p/\partial T)_{P,n_s,\alpha} \cong (\partial \ln p/\partial T)_{n_s,\alpha};$$

also

$$(\partial S_s/\partial n_s)_{P,T,\alpha} \cong (\partial S_s/\partial n_s)_{T,\alpha} \cong (\partial S_s/\partial n_s)_{V_s,T,\alpha}, \quad \text{etc.},$$

and furthermore,

$$(\partial H_s/\partial n_s)_{T,\alpha} \cong (\partial E_s/\partial n_s)_{T,\alpha}.$$

From Eq. (28) we obtain

$$(\partial p/\partial T)_{n_s,\alpha} = (s_G - \bar{s}_s)/(v_G - \bar{v}_s). \qquad (29)$$

In the usual approximation, $v_G \gg \bar{v}_s$, and assuming a perfect gas,

$$(\partial \ln p/\partial T)_{n_s,\alpha} = (s_G - \bar{s}_s)/RT. \tag{30}$$

At equilibrium, $\mu_G = \mu_s$, i.e., $f_G = \bar{f}_s = h_G - Ts_G = \bar{h}_s - T\bar{s}_s$, and therefore,

$$T(s_G - \bar{s}_s) = h_G - \bar{h}_s \equiv h_G - (\partial H_s/\partial n_s)_{T,P,\alpha}. \tag{31}$$

Also, n_s and α may be replaced in Eq. (30) by $\Gamma \equiv n_s/\alpha$, a surface concentration, since only the ratio, n_s/α, and not the total quantity of each is significant. Eq. (30) may, therefore, be written as

$$\left(\frac{\partial \ln p}{\partial T}\right)_\Gamma = \frac{h_G - \bar{h}_s}{RT^2} \equiv \frac{q_{st}}{RT^2}, \tag{32}$$

in which $h_G - \bar{h}_s \equiv q_{st}$ defines the isosteric heat of adsorption. It should be noted that, by convention, $\Delta h \equiv \bar{h}_s - h_G \equiv -q_{st}$.

Since $(\partial H_G/\partial p)_T = 0$ for a perfect gas, $h_G - \bar{h}_s$ corresponds to the enthalpy difference between one mole of perfect gas at any pressure and one mole of adsorbate in equilibrium with gas at pressure p. On the other hand, s_G is not independent of pressure and therefore $s_G - \bar{s}_s$ corresponds to the entropy difference between one mole of gas at equilibrium pressure p and one mole of adsorbate in equilibrium with that pressure.

There is nothing in Eq. (32) that restricts its application to systems with inert adsorbent. One can always use the equation to obtain heats of adsorption from experimental isosteres or isotherms, whether perturbations of the adsorbent exist or not. However, only in the absence of perturbations can significant interpretations of the data be made. Otherwise, the heat of adsorption is distributed in some unknown and complex manner between the adsorbate and adsorbent. Halsey (7) has discussed the formal thermodynamic equations in which a work term for perturbations is explicitly shown.

In order to show that q_{st} is actually the heat transferred to the constant temperature bath in an isothermal, isobaric process, we use

$$dQ = dE + p\,dV, \tag{33}$$

where $E = E_G + E_s$ and $V = V_G + V_s$. Setting $E_G = n_G e_G$, $E_s = n_s e_s$ and $dn_G = -dn_s$, while neglecting V_s, and remembering that e_G and v_G are constant, we find

$$\begin{aligned} dQ &= -e_G\,dn_s + n_s(\partial e_s/\partial n_s)_{\alpha,T}\,dn_s + e_s\,dn_s - pv_G\,dn_s \\ &= [(\partial E_s/\partial n_s)_{\alpha,T} - h_G]\,dn_s \cong [(\partial H_s/\partial n_s)_{\alpha,T} - h_G]\,dn_s \\ &\equiv -q_{st}\,dn_s. \end{aligned} \tag{34}$$

If there is more than one species adsorbing on the inert adsorbent, the energy differential becomes

$$dE_s = T\,dS_s - P\,dV_s - \varphi\,d\alpha + \sum_{i=1}^{m} \mu_{si}\,dn_{si}, \tag{35}$$