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459

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THE STRESS DEPENDENCE OF ADSORPTION

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ABSTRACT

Considering a gas-solid adsorption system, we present a simple analysis of the changes in the chemical potential of the adsorbed gas as the substrate solid is subjected to external forces. Using the canonical partition function, we show that the chemical potential varies with applied stress which variation we call the chemostress coefficient. Numerical values obtained for these coefficients indicate that the magnitude of the effect depends sensitively on the solid-gas interaction potential which in turn depends on the changes of the polarizabilities and of excitation energies of the solid.

INTRODUCTION

It has always been an open question in all branches of science whether in developing a theory to describe a given phenomenon one has taken into account the minimum number of fundamentally independent variables. Ideally the more number of such variables a theory is based on, the more detailed description must ensue from it so that these variables are not considered as "just some parameters to fit the data."

A remarkable example of discovery of such fundamental variables is the spin of an electron, and more such fundamental internal degrees of freedom have been discovered in elementary particle physics. On the classical statistical thermodynamic level one has derived guidance from, for example, the Gibbs phase rule. However, when we start considering non-equilibrium phenomena on a statistical physical level, we find that the classical phenomenological equilibrium thermodynamic concepts do not suffice to give the details that we want to obtain from the system under study. In this paper we shall take up the concept of the chemical potential that was considered by Gibbs but we shall generalize it so that it encompasses interactions that involve coupling between mechanical and chemical energy contents of the system. We shall see that the ordinary chemical potential so generalized will depend on mechanical stresses within a solid or at the gas-

82 07 20 158

solid interface.

The need for such a generalization arises in connection with a number of phenomena in which in fact a coupling of mechanical and chemical effects have been observed. Among these effects are: the Rebinder effect which shows a change in microhardness of a solid when the surface of the substance is in contact with certain classes of chemicals; the well known phenomenon of stress-corrosion which shows highly increased rate of corrosion of a substance in certain chemical environments and under stresses such that either the chemical or the stresses alone do not produce a significant rate of corrosion.

In a series of papers (ref. 1 to 6) we have derived expressions for the dependence of the chemical potential on stresses in solids for the adsorption phenomenon. This interaction, which we call the chemostress effect, now gives a level of detail of the dependence of this thermodynamic quantity on internal variables of the substances such as polarizabilities of the atom and the substance, phonon spectrum of the solid substrate, excitation spectra, band structure, interatomic potential characteristics, variation of these with pressure, etc. Such details which tie the adsorption phenomena to chemical and physical specificities of the species involved were not available in previous theories.

Furthermore, a number of specific new experiments that need be carried out for new quantities that come out of this theory are shown in these papers. Among these we mention a few here such as the change of heat of adsorption with stress, extension of the "Jarman Rule" of polarization from alkali halides to other solids, variation of phonon and excitation spectra with stress.

Another aspect of the theory is that it becomes a fertile ground for testing several other theories such as the theory of ionicity, oxidation theories, hydrogen embrittlement.

Because we have discussed in previous publications (ref. 1-6) details of several methods of calculating the chemostress coefficient and because the need exists to extract from these publications the minimal theoretical conclusions that still supports the existence of this chemostress effect, we shall now give a brief presentation of the simplest of these theoretical treatments below.

A comprehensive review of the statistical thermodynamics of adsorption has been given by Steele (ref. 7). We make extensive use of the works of Steele and Halsey (ref. 8), Freeman and Halsey (ref. 9), Sams, Constabaris and Halsey (ref. 10) and of some of the more general findings of Steele (ref. 11). The present study refers not to the dependence of the chemical potential μ on the pressure of the adsorbed gas but on the stresses applied to the solid substrate. Nor does the present study concentrate on the specificities that would be associated with particular gas-substrate systems, specificities that would result from details of the interatomic potential peculiar for each system, the crystallographic orientation of the surface, degree of imperfections within the solid and on the

surface, etc. Such a detailed study of special classes of metals, ionic solids, etc. with specified imperfections is deferred to the future. Rather, the significant point of the present analysis is the result that even with a rather idealized solid or a non-metal, the chemical potential of the adsorbed gas may vary 1-10% with moderately high pressures of the order of 3-8 kilobars applied to the solid. It remains to be seen whether imperfections in the solid increase or decrease the magnitude of this chemostress effect. We argue that within the limits of this uncertainty, this coefficient, or rather this tensor (since it depends on crystal-line surface orientation and the tensorial nature of the stresses) may be a non-negligible quantity. We also emphasize that the chemostress effect need not be confined to physisorption and chemisorption processes alone, that it is a more general effect.

THE CHEMICAL POTENTIAL FOR ADSORBED GAS

Starting with the canonical ensemble, expressions for the variation of the chemical potential with stress, which we shall call the chemostress coefficient, will be derived. The numerical results obtained below show that the interaction potential between gas and the substrate atoms needs further careful investigation, specifically in connection with rather general classes of substrate solids which have ionic, metallic or other bonding characteristics.

Using the canonical partition function one obtains, as usual, an expression for the chemical potential μ_i of the i -th component

$$\mu_i = -kT \left(\frac{\partial \ln Z}{\partial N_i} \right)_{T,V,N_j} \quad (1)$$

$$\text{where } Z = e^{-F/kT} \quad (2)$$

$$= \sum_v e^{-E_v/kT} \quad (\text{classical}) \quad (3)$$

Z being the partition function, F the Helmholtz free energy, T the temperature, V the volume, N_j the number of molecules of the j -th species (component); E_v refers to the energy eigenvalue of the v -th state associated with the Hamiltonian H of the appropriate Schrodinger equation of the system in the quantum mechanical partition function

$$Z = \frac{1}{h^\phi} \int \dots \int e^{-H/kT} dv_q dv_p \quad (4)$$

ϕ being the number of degrees of freedom of the system.

For the present problem, the potential energy U in the Hamiltonian

$$H = \sum_{i=1}^3 \frac{p_i^2}{2m} + U(q_1, \dots, q_N) \quad (5)$$

is the total effective interaction potential between the N gas molecules and the solid substrate taken as a whole.

The passage from quantum statistical mechanics to classical statistical mechanics referred to above in terms of the respective partition functions leads to a corresponding transition in the Helmholtz free energy

$$F_{\text{quantum mechanical}} \rightarrow F_{\text{classical}} \quad (6)$$

thereby forcing the following factorization

$$e^{-F_{\text{class.}}/kT} = e^{-F_{\text{ideal}}/kT} \cdot e^{-F_{\text{config}}/kT} \quad (7)$$

$$\text{with } Z_{\text{class.}} = Z_{\text{ideal}} \cdot Z_{\text{config.}} \quad (8)$$

$$\text{where } Z_{\text{config.}} = \frac{Q}{V^N} \quad (9)$$

$$\text{and } Q \equiv \int \dots \int e^{-U/kT} dq_1 \dots dq_N. \quad (10)$$

Here Q is the usual "configurational integral", the kinetic energy part of the Hamiltonian having gone into Z_{ideal} .

We know (ref. 13) that the chemical potential of the non-ideal systems breaks up as

$$\mu = \mu_{\text{ideal}} + \tilde{\mu} \quad (11)$$

where $\tilde{\mu}$ is the part arising from interactions that do not appear in the ideal system; thus

$$\frac{\mu_i}{kT} = - \left(\frac{\partial \ln Z_{\text{ideal}}}{\partial N_i} \right)_{T,V,N_j} - \left(\frac{\partial \ln Z_{\text{config.}}}{\partial N_i} \right)_{T,V,N_j} \quad (12)$$

Since we are interested only in the deviation of the gas adatoms from ideal behavior and beyond that in the variation of this deviation with applied stress--which would arise from a corresponding change in the configurational integral--we need only

$$\frac{\mu}{kT} = - \left(\frac{\partial \ln Z_{\text{config.}}}{\partial N_1} \right)_{T,V,N_j} \quad (13)$$

$$= - \left[\frac{\partial \ln (Q/V^N)}{\partial N_1} \right]_{T,V,N_j} ; \quad (14)$$

we note thereby the origin of the factor V^N that appears in this expression. The validity of this passage to the classical limit rather than the use of the "Slater sum" (ref. 7) is rather doubtful when the solid substrate is compressed or more generally when stresses are applied to it. This is so since the band structure of the solid can change considerably involving changes in the ground state and furthermore excitations to higher levels. Higher states thus may contribute to changes in the polarizabilities of the solid which, as we shall see, can alter the interaction potential. However, in harmony with our goal which is to show that a chemostress effect may exist based on general grounds, we shall use this classical limit.

The interaction potential U is usually regarded as being made up of two-body interactions between any adatom and each of the atoms of the solid substrate. Furthermore it is assumed that the total potential is additively (ref. 14) made up from these. While this assumption may yield a fair approximation to the actual interaction for extreme ionic solids, it certainly fails for metal substrates. For these one needs to use image potentials which are further corrected (ref. 15) for effects which become rather significant at close distances between the adatom and the metal substrate. In any case, there will be an effective interatomic potential u_i between the i -th adatom and the solid substrate taken as a whole. Denoting by u_{ij} the effective interaction between any two gas molecules and neglecting higher order terms we have

$$U = \sum_{i=1}^N u_i + \sum_{j>k}^N \sum_{k=1}^{N-1} u_{jk} . \quad (15)$$

As usual, (ref. 16) one defines the functions:

$$f_i \equiv e^{\frac{-u_i/kT}{-1}} \quad (16)$$

$$f_{ij} \equiv e^{\frac{-u_{ij}/kT}{-1}} \quad (17)$$

in terms of which the configurational part of the partition function becomes

$$Z_{\text{conf.}} = \frac{Q}{V^N}$$

$$= \left(1 + \frac{B_{AS}}{V}\right)^N \left[1 + \frac{N(N-1)}{2} \cdot \frac{C_{AAS}}{(V+B_{AS})^2} + \dots\right] \quad (18)$$

where

$$B_{AS} = \int_V f_1 dr_1 \quad (19)$$

$$C_{AAS} = \iint_V (1+f_1)(1+f_2) f_{12} dr_1 dr_2 \quad (20)$$

Here we pause to examine the meaning of the volume V that appears above. As discussed by Steele (ref. 7), the volume V can be divided into two parts; a part V_a which is a small volume near the surface where the gas density is appreciably different from the density in the remainder (ref. 7) $V-V_a$ of the volume V ; then the main contribution of Eq. 18 comes from V_a . Denoting the totality of the surface of the solid by A ,

$$V_a = A \cdot \tilde{h} \quad (21)$$

where h is a derived distance beyond which the interatomic potential at the temperature T of the system has no effect. Another way of stating this is that beyond a perpendicular distance $\tilde{h}$ away from surface, the attractive part of the potential is significantly less than kT below the zero of the potential that was taken to be at infinity, and therefore these molecules are essentially free from the u_1 interaction.

Another parameter that is significant is the distance z_0 of closest approach between adatoms and the solid atoms. This is usually taken to be approximately where the repulsive part of the potential intersects the z axis that is perpendicular to the surface.

Neglecting, for the present analysis, the C_{AAS} and higher order contributions, we obtain

$$\frac{\mu}{kT} \approx - \ln \left(1 + \frac{B_{AS}}{V_a}\right) \quad (22)$$

Using the experimentally and theoretically determined (ref. 10,11) ratio

$$\eta \equiv \frac{B_{AS}}{A \cdot z_0} \quad (23)$$

Eq. 22 becomes

$$\frac{\mu}{kT} = - \ln \left(1 + \frac{z_0}{\tilde{h}} \eta\right) \quad (24)$$

and we see in Fig. 1 that $\tilde{\mu}$ is sensitively dependent on the magnitude of the minimum of the potential denoted by ϵ^* which is the heat of adsorption. We see from Fig. 2 that the dependence of η on ϵ^* is insensitive to the powers of inverse-power-law interaction potentials and that $\log \eta$ is linearly dependent on ϵ^* . One may again question the validity of such general conclusions but we accept it since we are seeking an "average thermodynamic" effect.

From Fig. 10-1 of Reference 7 we observe that h is a small multiple of z_0 and therefore $\tilde{\mu}$, or $\exp[-\tilde{\mu}/kT]$ which is a more significant quantity, becomes sensitive to variations of the depth ϵ^* of the potential.

THE CHEMOSTRESS EFFECT

In this section we show that stresses applied to the solid may change the chemical potential.

A variety of interatomic potentials proposed for physical adsorption have been reviewed by Margenau (ref. 14). For extreme ionic solids, additivity of the two-body interaction between adatom and substrate atoms can be assumed to be approximately valid, giving the result

$$U \approx \frac{1}{4} \pi D^{-3} \alpha_a \alpha_s \cdot \frac{\bar{E}_a \cdot \bar{E}_s}{\bar{E}_a + \bar{E}_s} \quad (25)$$

where D is the perpendicular distance between the adatom and the solid surface, α_s and α_a are the polarizabilities of the solid and of the adatom respectively; $\bar{E}_a$ is the mean excitation energies of the adatom and $\bar{E}_s$ is that of the solid. Applied stresses can change the polarizabilities of the solid (ref. 17). In the range of 3-10 kilobars, the empirical Jarman rule (ref. 18)

$$\frac{V}{\alpha} \left(\frac{\partial \alpha}{\partial V} \right)_T \approx 2.0 \quad (26)$$

seems to hold for alkali halides in general, where α is the polarizability and V the volume of the solid. This translates to

$$\frac{\Delta \alpha}{\alpha} \approx 2.0 \beta (\Delta P) \quad (27)$$

where ΔP is the pressure change and β is the isothermal compressibility

$$\beta \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (28)$$

For example, for NaCl, 2% change in volume for ~10 kilobar increase in pressure appears to be (ref. 19) a reasonable order of magnitude estimate based on experimental data. Therefore a change of

$$\frac{\Delta\alpha}{\alpha} \approx 0.04 \quad (29)$$

may result in the polarizability. Referring to Eq. 25 above, if one neglects variations of $\bar{E}_s$ with pressure for the moment (to be discussed below), a fractional change of 4% in the polarizability translates into a similar change in the depth of the potential, i.e., the heat of adsorption in this case. The experimental findings of Sams et al (ref.10) then clearly indicate that $\ln(B_{AS}/Az_o)$ varies linearly with ϵ^*/RT giving approximately a 20% change in B_{AS}/Az_o , if we assume that these experimental findings of Sams et al. can be extended to alkali halides; this is a rather strong assumption that is partly based on the insensitivity, mentioned above, of this dependence on the exponents of the Lennard-Jones type potential as well as on the universality of a law suggested by the results shown in Fig. 1.

Combining these results, we have

$$-\frac{\Delta\mu}{\Delta\sigma} \approx \frac{z_o/\bar{h}}{1+(z_o/\bar{h})\eta} \frac{\partial\eta}{\partial\sigma} \quad (30)$$

where σ stands for a general form of stress whose tensorial aspects are here neglected in line with the purpose of the present paper. Depending on the values chosen, this then may give a 1-10% effect.

There remains the question of the variation of the mean excitation energy $\bar{E}_s$ of the solid with applied stress. We do not know at this stage whether this change (which can exist due to changes in the band structure when the solid is stressed) would increase or decrease the magnitude of the chemostress effect. In any case we know that these two variations may be intertwined and at high pressure one may not be allowed to assume

$$\frac{\partial U}{\partial\sigma} \approx \frac{\partial U}{\partial\alpha} \frac{\partial\alpha}{\partial\sigma} + \frac{\partial U}{\partial\bar{E}_s} \frac{\partial\bar{E}_s}{\partial\sigma}, \quad (31)$$

namely, the separability of the two contributions. This brings us back to the question of the validity of the pairwise additivity of the interatomic potential. Considering even the possibility of insulator-metal type transitions under high pressures, we want to go from solids with ionic bonding to metals and see whether in this latter extreme the chemostress effect may also be observable. We use Bardeen's (ref. 15) result for the van der Waals interaction between a neutral molecule and a metallic surface.

$$U = - \frac{e^{2\langle r \rangle}}{12D^3} \frac{Ce^2/2r_s}{\bar{E}_s + (Ce^2/2r_s)} \quad (32)$$

where r_s is the radius of a sphere whose volume is equal to the volume occupied

per electron in the metal. A change in volume then translates into a change in the van der Waals attractive part of the interaction potential and therefore in the minimum of the total potential which includes a repulsive part. Although C itself depends on r_s , one may assume this to be a weak dependence and that $Ce^2/2r_s$ is of the order of magnitude unity. Thus a few percent change in r_s gives a similar change in ϵ^* to within a factor of two. It appears then that a chemostress effect may be expected in most solids on general grounds.

It must be emphasized, however, that in a real solid under stress, dislocations are generated whose dynamics (such as migration to the surface) should alter the effective "average" dispersion forces. It would require rather extensive studies to separate out the contributions to changes of heat of adsorption that come indirectly from such imperfections. However, no matter what the detailed mechanisms and the particular pathways may be, if the heat of adsorption is changed under stress, then there will be a corresponding change in the chemical potential, indicating that the chemostress coefficient may be a non-negligible entity.

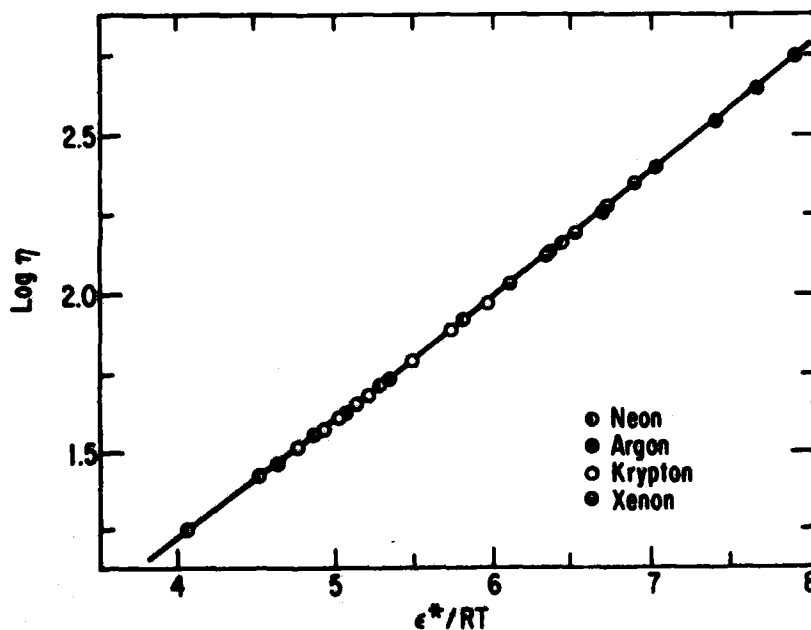


Fig. 1. Fit of the experimental results of the 3-12 potential model (see reference 10).

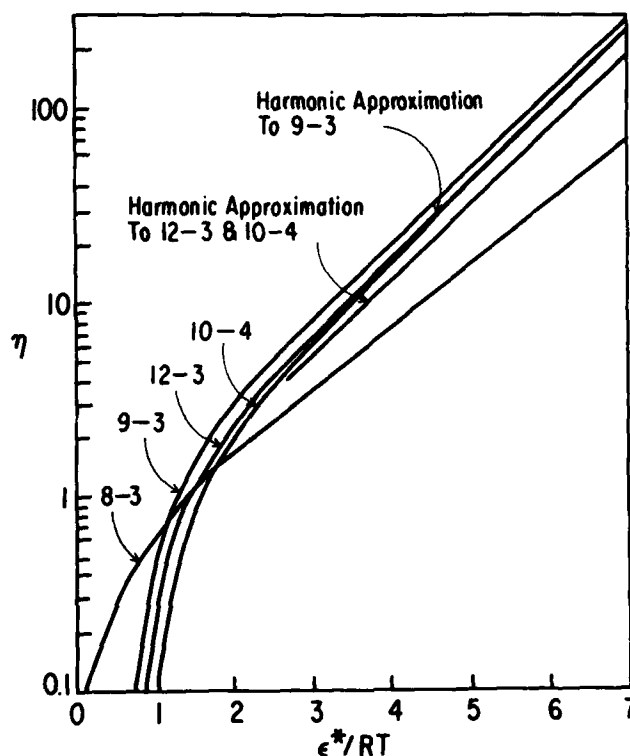


Fig. 2. Theoretical dependence of η on ϵ^*/RT for various power-law interaction functions (see references 10 and 7).

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