A DESCRIPTION OF THE GAS–SOLID INTERFACE

J. A. POULIS[†], J. M. THOMAS[*], and C. H. MASSEN[†]

[†]*Physics Department, Eindhoven University of Technology, Eindhoven (The Netherlands)*
[*]*Chemistry Department, University of Wales, Aberystwyth (Great Britain)*

(Received April 3rd, 1972)

ABSTRACT

It was Wiedemann who demonstrated the relevance of adsorption phenomena in thermo-analytical research. In the present paper a contribution is given to analyse in how far the commonly used word "adsorption" covers the adsorption phenomena encountered in the measurement procedure of thermogravimetry. The practical definition of adsorption both from volumetric and gravimetric methods is compared with a definition from a gas kinetical treatment. It is shown that the difference between the definitions is not always negligible.

INTRODUCTION

Adsorption is a phenomenon which plays a role in most experiments in the fields of thermogravimetry[1,2] and thermoanalysis. In these fields adsorption is not always only a disturbing effect, which has to be eliminated by pumping and baking out procedures, but the adsorpion state can be of essential importance, for instance, as an intermediate state in solid–gas reactions and in diffusion of gases in solids.
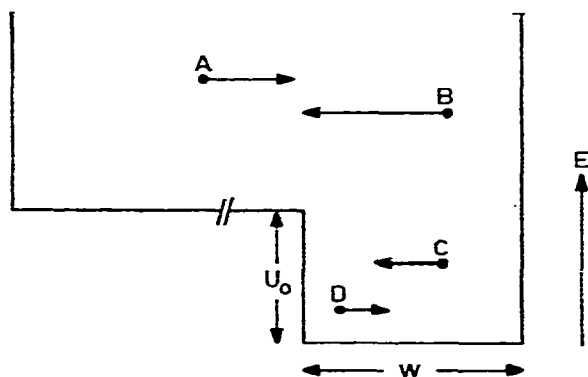

Fig. 1. The potential energy curve used.

2

In different approaches of adsorption, it may be easiest to use different defini-
tions for "adsorbed molecule" and for "number of adsorbed molecules". It is the
aim of the present paper to compare the different definitions and to analyse the magni-
tude of the errors which can be involved through inappropriate use of the definitions.
The treatment will be set up along the lines of the kinetic theory of gases. The following
simplifications are made: (*1*) Gas molecules are supposed to collide with the walls
only, so collisions between the gas molecules are neglected. (*2*) The interaction between
gas molecules and the walls is characterised by a rectangular potential well of width
w and depth U_0 (see Fig. 1). (*3*) Only the movements of the molecules in directions
perpendicular to the walls are considered.

In Fig. 1 four molecules are shown. The molecules A and D will have their
next collision with the real wall at the right-hand side of the figure. Molecule B will
escape from the potential well, but molecule C will be reflected by the potential wall
and then return in the direction of the real wall with unchanged kinetic energy. From
this picture we learn that three kinds of molecules can be distinguished on the basis
of their presence in one of the three regions α, β and γ, as drawn in Fig. 2. As the
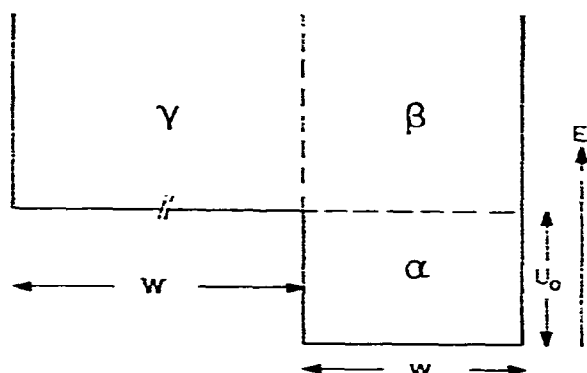

Fig. 2. Molecular regions in the theoretical procedure.

molecules in region α do not have sufficient energy to escape from the potential well,
these molecules are called adsorbed in the kinetic treatment. We will refer to this as
the molecular definition of adsorption.

EXPERIMENTAL

Gravimetric experiments

Here we shall consider the role of adsorption in thermogravimetry. In Fig. 3,
a sample is shown suspended from a balance, the volume of the sample is V_s, and
its density ρ_s. $V_{\alpha\beta}$ is the volume around the sample in which adsorption occurs, so
$V_{\alpha\beta}$ corresponds with the α- and the β-region, as shown in Fig. 2, together. When the
mass of the α, β and γ molecules in a unit volume is called ρ_α, ρ_β and ρ_γ, respectively,

the force F_g, due to gravity on the sample and the gas molecules present in $V_{\alpha\beta}$, is given by

$$F_g = g\{V_s\rho_s + V_{\alpha\beta}(\rho_x + \rho_\beta)\} \tag{1}$$

where g is the acceleration due to gravity.

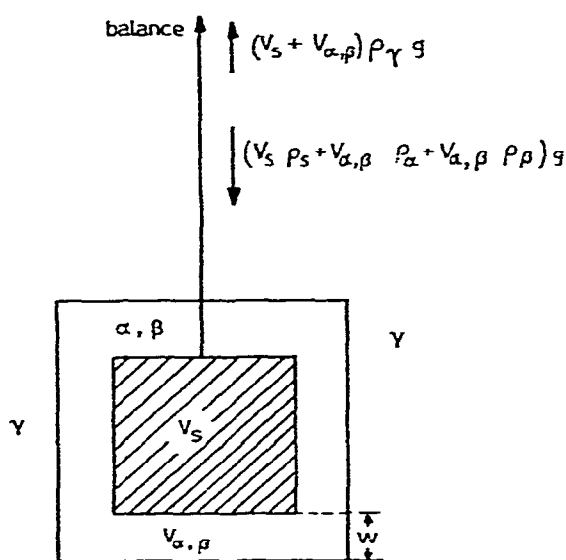

Fig. 3. Molecular regions in the gravimetric procedure.

The buoyancy force, F_b, amounts to

$$F_b = g(V_s + V_{\alpha\beta})\rho_\gamma \tag{2}$$

The net force F_t acting on the balance is

$$F_t = F_g - F_b = g\{V_s(\rho_s - \rho_\gamma) + V_{\alpha\beta}(\rho_x + \rho_\beta - \rho_\gamma)\} \tag{3}$$

where the term $gV_{\alpha\beta}(\rho_x + \rho_\beta - \rho_\gamma)$ represents the experimental effect caused by the adsorption.

Volumetric experiments

A volumetric set-up is schematically shown in Fig. 4. A vessel (volume V_t) containing a solid sample (volume V_s) is originally evacuated. An amount of gas, mass M, is let into the vessel. This gas splits up into two regions, namely the adsorbtion region (volume $V_{\alpha\beta}$) around the sample and the rest of the space with volume V_γ, satisfying the equation

$$V_\gamma = V_t - V_s - V_{\alpha\beta} \tag{4}$$

For the distribution of the mass of the gas the following equation holds

$$M = (V_t - V_s - V_{\alpha\beta})\rho_\gamma + V_{\alpha\beta}(\rho_x + \rho_\beta) \tag{5}$$

which upon rearranging gives

$$M = (V_t - V_s)\rho_7 + V_{\alpha\beta}(\rho_\alpha + \rho_\beta - \rho_7) \tag{6}$$

In Eqn. (6), the term $V_{\alpha\beta}(\rho_\alpha + \rho_\beta - \rho_7)$ refers to the measured amount of adsorbed gas.
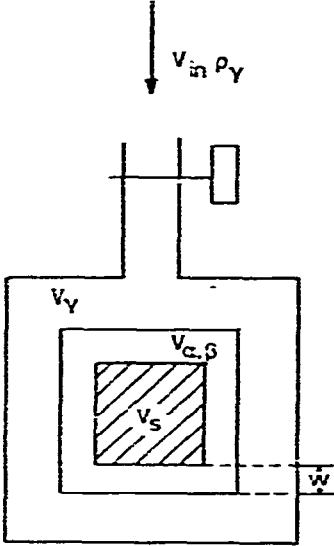

Fig. 4. Molecular regions in the volumetric procedure.

DISCUSSION

Qualitative comparison

The number of adsorbed molecules (n_α) according to the molecular definition amounts to

$$n_\alpha = \frac{1}{m} V_{\alpha\beta}\rho_\alpha \tag{7}$$

where m stands for the mass of one molecule.

In a similar way, the numbers of molecules, n_β and n_γ, in the β and γ regions, respectively are defined as

$$n_\beta = \frac{1}{m} V_{\alpha\beta}\rho_\beta \tag{8}$$

and

$$n_7 = \frac{1}{m} V_7\rho_7 \tag{9}$$

It follows from Eqns. (3) and (6) that in the gravimetric and volumetric experiments, the number n_p of adsorbed molecules amounts to

$$n_p = \frac{1}{m}\, V_{\alpha\beta}(\rho_\alpha + \rho_\beta - \rho_\gamma) \tag{10}$$

We shall refer to Eqn. (10) as the "practical" definition of the number of adsorbed molecules.

Using Eqns. (7), (8) and (9) in Eqn. (10) leads to

$$n_p = n_\alpha + n_\beta - \frac{V_{\alpha\beta}}{V_\gamma}\, n_\gamma \tag{11}$$

We see from Eqn. (11) that there is a difference between n_p and n_α, which means that the "practical" and the "molecular" definitions are not identical.

Apart from this there is another basic difference: the molecular definition enables us to say whether or not a molecule is an adsorbed one. This is not so for the practical definition, where only the total number of adsorbed molecules is defined, but where no adsorption criterium for individual molecules can be given.

Returning to Eqns. (7) and (10), we see that the difference between n_p and n_α originates from the difference between ρ_β and ρ_γ. For the explanation of this, let us consider two planes both parallel to the wall, the first inside, the second outside, the adsorption region. The number of β molecules passing through the first plane in each of the two directions equals the number of γ molecules passing the second plane in the same direction, when stationary state conditions are assumed. In other words, the "flow densities" in the β and γ regions are equal to one another.
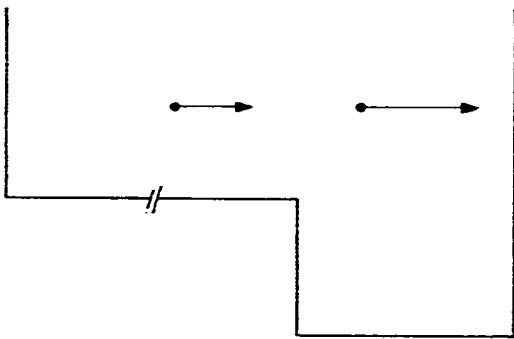

Fig. 5. Illustration of the difference in velocity caused by the potential energy jump.

In Fig. 5, it is illustrated that a molecule travelling from the γ to the β region looses potential energy when passing the boundary between the two regions. This must be accompanied by an increase of the kinetic energy, and therefore of the velocity, of the molecule. This explaines the fact that, though the "flow densities" in the β and γ region have the same value, the densities are not equal to one another.

6

Quantitative comparison

In this section, we shall give a quantitative treatment of the difference between n_p and n_z, which has already been qualitatively explained above. The calculations can be carried out in different ways. The way chosen in the present paper is one which, though here applied for a rectangular potential well, can in principle be used for any other form of potential energy curve [3,4]. In the calculations, use will be made of the width, W, of the vessel, shown in Fig. 2, where it can also be seen that only one end of the vessel is supposed to take part in the adsorption process, as the opposite wall is represented by an energy jump of infinite height.

Using the equations

$$V_{z\beta} = Aw \tag{12}$$

where A stands for the surface area of the sample, and

$$V_\gamma = AW \tag{13}$$

equation (11) reads

$$n_p = n_z + n_\beta - \frac{w}{W} n_\gamma \tag{14}$$

We shall evaluate this relation by expressing n_β and n_γ in terms of n_z. We define the oscillation time τ as the time interval it takes a gas molecule which leaves the wall to return to it, while on its way its total energy remains constant. So for z molecules $(0 < E < U_0)$ the oscillation time $\tau_z(E)$ reads

$$\tau_z(E) = w\sqrt{(2m/E)} \tag{15}$$

To find the oscillation time $\tau_{\beta + \gamma}(E)$ for the other molecules $(E > U_0)$, we have to consider that during a part of this oscillation time, these molecules are β molecules [during $\tau_\beta(E)$ sec.] and that during the rest of their oscillation time, they are γ molecules [during $\tau_\gamma(E)$ sec], so

$$\tau_{\beta + \gamma}(E) = \tau_\beta(E) + \tau_\gamma(E) = w\sqrt{(2m/E)} + W\sqrt{(2m/E - U_0)} \tag{16}$$

These oscillation times we can make use of when calculating the density of the energy levels as a function of energy. The formal approach for the calculation of this density would be to solve the eigenvalue problem of Schrödinger's equation, but using the Heisenberg relation, this can be connected with the classical oscillation times. When $g(E)dE$ is the number of energy levels between E and $E+dE$, the Heisenberg relation reads here

$$\tau(E) \frac{1}{g(E)} = h \tag{17}$$

where h is Planck's constant.

For $0 < E < U_0$, it follows from Eqns. (15) and (17) that

$$g(E) = \frac{w}{h}\sqrt{(2m/E)} \tag{18}$$

For $E > U_0$, it is follows from Eqns. (16) and (17) that

$$g(E) = \frac{w}{h}\sqrt{(2m/E)} + \frac{W}{h}\sqrt{(2m/E - U_0)} \tag{19}$$

Letting $n(E)dE$ be the number of molecules with an energy between E and $E + dE$ then, using Boltzmann statistics, it follows that for $0 < E < U_0$

$$n_\alpha(E) = C\frac{w}{h}\sqrt{(2m/E)}\,e^{-E/kT} \tag{20}$$

where C is a constant which may be calculated by applying the usual normalising procedure.
Similarly, for $E > U_0$ we find

$$n_{\beta\gamma}(E) = C\{\frac{w}{h}\sqrt{(2m/E)} + \frac{W}{h}\sqrt{(2m/E - U_0)}\}\,e^{-E/kT} \tag{21}$$

The number of molecules $n_{\beta\gamma}(E)dE$ with energy between E and $E + dE$, while $E > U_0$, we shall split up into the numbers $n_\beta(E)dE$ and $n_\gamma(E)dE$, being the numbers of molecules with energies between E and $E + dE$, in the β and the γ region, respectively. For these numbers we now, incorporating Eqn. (16)

$$\frac{n_\beta(E)}{n_\gamma(E)} = \frac{\tau_\beta(E)}{\tau_\gamma(E)} = \frac{w\sqrt{(2m/E)}}{W\sqrt{(2m/E - U_0)}} \tag{22}$$

from Eqns. (21) and (22) it follows that

$$n_\beta(E) = C\frac{w}{h}\sqrt{(2m/E)}\,e^{-E/kT} \tag{23}$$

$$n_\gamma(E) = C\frac{W}{h}\sqrt{(2m/E - U_0)}\,e^{-E/kT} \tag{24}$$

Integration over the energy regions involves yields

$$n_\alpha = \frac{Cw\sqrt{2m}}{h}\int_0^{U_0} E^{-\frac{1}{2}}\,e^{-E/kT}\,dE \tag{25}$$

$$n_\beta = \frac{Cw\sqrt{2m}}{h}\int_{U_0}^{\infty} E^{-\frac{1}{2}}\,e^{-E/kT}\,dE \tag{26}$$

$$n_\gamma = \frac{CW\sqrt{2m}}{h} \int_{U_0}^{\infty} (E - U_0)^{-\frac{1}{2}} \, e^{-E/kT} \, dE \tag{27}$$

For numerical evaluation of the above integrals we shall rewrite them in terms of error functions defined as:

$$\mathrm{erf}(t) = \frac{2}{\sqrt{\pi}} \int_0^t e^{-y^2} \, dy \tag{28}$$

This leads to

$$n_z = C \cdot \frac{w}{h} \sqrt{(2\pi mkT)} \, \mathrm{erf}\{\sqrt{(U_0/kT)}\} \tag{29}$$

$$n_\beta = C \cdot \frac{w}{h} \sqrt{(2\pi mkT)} \{1 - \mathrm{erf}\{\sqrt{(U_0/kT)}\}\} \tag{30}$$

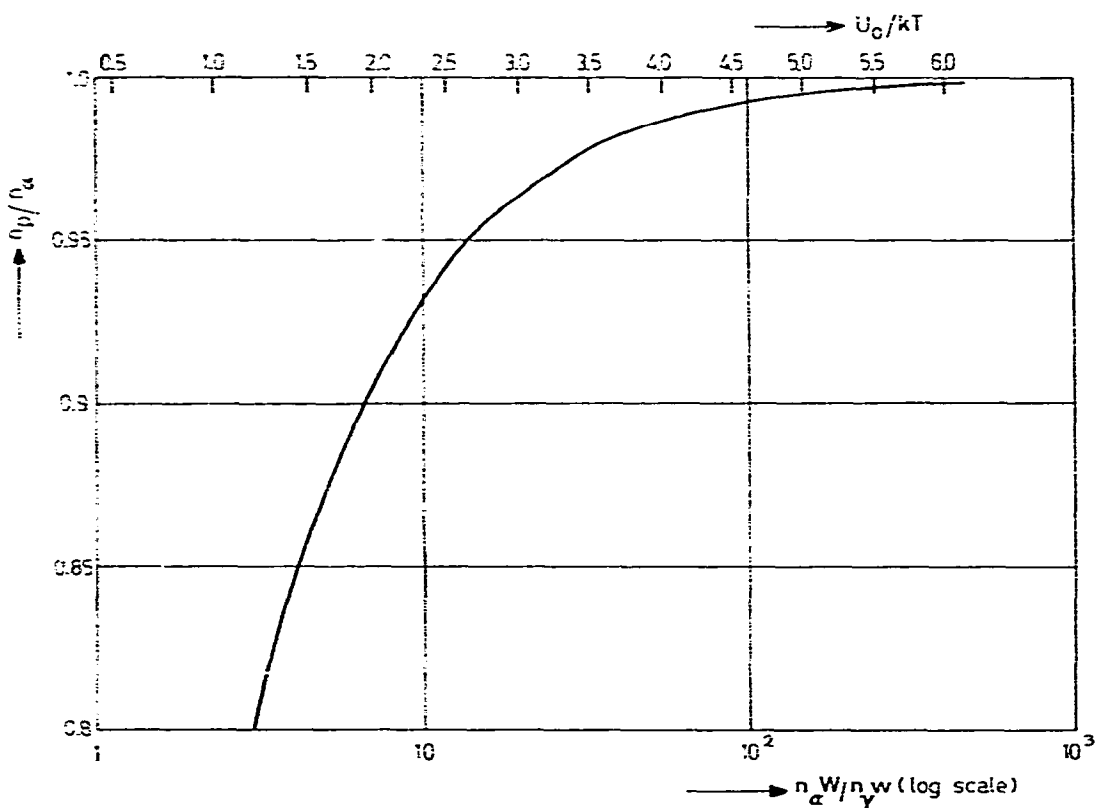$$n_\gamma = C \cdot \frac{w}{h} \sqrt{(2\pi mkT)} \, e^{-U_0/kT} \tag{31}$$

Fig. 6. The quotient of the two number of adsorbed molecules as a function of the relative adsorption.

From the three Eqns. (29), (30) and (31), one can solve three unknown quantities. Taking for these quantities n_β, C and T, one can express these in terms of n_x and n_{z}. Using these solutions in Eqn. (14), gives a relation between n_z, n_z and n_p. This relation can be rearranged as one between n_p/n_x and $(n_x W)/(n_z w)$. The latter relation is represented in Fig. 6.

We see that for $(n_x W)/(n_z w) > 10$, the difference between n_x and n_p is less than 7%. From the scale on the top of Fig. 6, we see that this is the case for $U_0/(kT) > 2.3$. For a typical chemisorption this latter inequality is valid in practically all experiments. For physical adsorption this inequality is only invalid in very high-temperature experiments. For the study of baking out procedures the effect should well be accounted for.

REFERENCES

1 H. G. Wiedemann, in C. H. Massen (Ed.), *Vacuum Microbalance Techniques*, Vol. 7, Plenum Press, New York, 1970, p. 217.
2 C. Duval, *Inorganic Thermograrimetric Analysis*, Elsevier, Amsterdam, 1963.
3 J. H. de Boer, *Electron Emission and Adsorption Phenomena*, Cambridge University Press, New York, 1935.
4 J. A. Barker and D. H. Everett, *Trans. Faraday Soc.*, 58 (1962) 1608.