PHYSICS OF OUTGASSING

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Abstract
This paper relates the physical bases of the gassing phenomena in ultra-high vacuum. The main phenomena discussed are: diffusion of gases through system walls and solids in vacuum, solubility of gases on solids and permeation as well as the phenomena of adsorption, desorption and absorption.

1. INTRODUCTION

It has been recognised for many years that gassing and outgassing are processes controlling the ultimate pressure and gas composition in high- and ultra-high vacuum systems [1, 2]. The mechanisms to stimulate outgassing are diverse:

(i) Thermal desorption.

(ii) Desorption induced by electronic transitions.

(ii) Vaporisation of materials.

(iv) Gas diffusion from the bulk and subsequent desorption.

(v) Gas permeation through the walls.

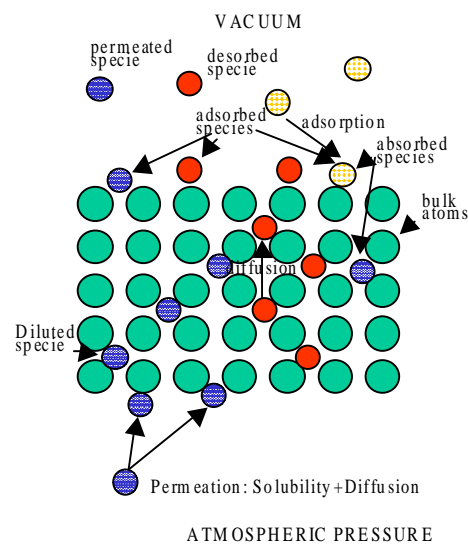In Fig. 1 the several mechanisms producing outgassing have been depicted.

Fig. 1 Surface and bulk phenomena in vacuum.

2. PERMEATION OF GASES THROUGH MATTER

Gases permeate through most materials, so gases present in the ambient air can permeate to vacuum chambers through the system walls. Permeation of gases is a combination of two physical processes: dissolution and diffusion. First, the gas **dissolves** in the solid and then it **diffuses** to the inner wall of the system. When the gas arrives at the inner surface, it **desorbs** to the vacuum volume.

The dissolution phenomenon obeys Henry's law:

$$c = sP^n$$

where c is the concentration, P the gas pressure, s the solubility, and n depends on the material and is 1 for non-metals. Diatomic molecules dissociate upon dissolving.

The concentration is measured in mbar.l or Pa.m^3 and it is the amount of gas expressed in mbar.l or Pa.m^3 measured at 293 K that dissolves in 1l or 1 m^3 of substance. s is the amount of gas measured in STP that dissolves in 1 l or 1 m^3 of substance at a pressure of 1033 mbar or 1.033×10^5 Pa, for $n = 1$ it is dimensionless and for $n = 1/2$ it has the dimensions of mbar$^{0.5}$ or Pa$^{0.5}$. After dissolving, the gas diffuses to the inner wall of the system according to Fick's first law of diffusion, for the stationary case. The gas flow, Q, through an area of unit cross section and time unit, is given by:

$$Q = -D\frac{dc}{dx}$$

where D is the diffusion coefficient, which depends exponentially on temperature.

$$D = D_0 e^{\left(-\frac{E}{kT}\right)}$$

where k is the Boltzmann constant; E is the activation energy for diffusion, T is the wall temperature and D_0 is a coefficient of proportionality.

We consider a wall of thickness d and very large area and at time $t = 0$, the two lateral surfaces are exposed to pressures P_1 and P_2. The concentrations on both faces due to solubility will be:

$$c_1 = sP^n \quad c_2 = sP^n$$

In addition, the gas flow will be:

$$Q = \frac{Ds\left(P_1^n - P^n\right)}{d}$$

where $n = 1$ for non-metals, and $n = 1/2$ for diatomic molecules in metals. $Ds = K$ is the permeation constant.

As the equilibrium is reached in many cases after a long period of time, so the transition regime is determined by applying Fick's second law:

$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}.$$

This equation can be solved for specific cases useful in vacuum technology.

Let's consider a wall as before with the following boundary conditions:
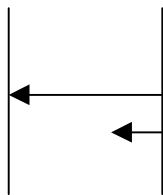
$c = 0$	$0 < x < d$	$t = 0$	$P = P_1 \quad P_2 = 0$
$c = c_1$	$x = d$	$t > 0$	
$c = 0$	$x = 0$	$t > 0$	

The total amount of gas permeated into the vacuum is given by:

$$Q = \frac{c_1 D}{d}\left(t - \frac{d^2}{6D}\right)$$

and the time constant:

$$t_a = \frac{d^2}{6D}$$

is the required time where Q is valid. This time constant is important to determine D. By representing Q as a function of t, the value of t_a can be determined by extrapolating the straight line and then D can be found. Table 1 summarises the permeation properties of some materials and it can be seen that elastomers should be avoided at pressures lower than 10^{-6} due to the high permeation rates for most

gases, helium permeation is important only in glass systems while gas permeation is not of importance in metal systems at room temperature except for H_2 but this gas is not in high concentrations in air.

Table 1
Permeation of gases through materials [3]

| Metals	Semiconductors	Polymers	Glasses
Rare gases do not permeate. H_2: high rate through palladium, through Fe by corrosion and electrolysis. O_2: permeates Ag. Permeation rates vary as (pressure)$^{0.5}$.	He and H_2 through Ge and Si. Ne and A not measurable. H_2 varies as (pressure)$^{0.5}$.	All gases permeate all polymers. Water rate high. Many particularities with the material. All rates vary as (pressure)$^{0.5}$.	H_2, He, D_2, Ne, A, O_2 are measurable through SiO_2. Vitreous silica. All rates vary as (pressure).

Table 2 shows an example of the permeation of an O-ring of standard dimensions: 0.5-m length and 4-mm diameter for the indicated materials. The O-ring when compressed takes a squared form 7-mm thick by 2-mm high so that the area of permeation is $0.5 \text{ m} \times 0.002 \text{ m}^2$.

Table 2
Permeation of air through an O-ring

MATERIAL	Permeation constant at 20ºC (mbar.l.s^{-1}.mm.m^{-2}.bar^{-1})	Air rate (mbar.l.s^{-1})	Ultimate pressure with a 1000 l/s pump (mbar)
Perbunam	2×10^{-2}	$2 \times 10^{-2} \times 0.002 \times 1/8 = 5.0 \times 10^{-6}$	5.0×10^{-9}
Viton	3×10^{-3}	$3 \times 10^{-3} \times 0.002 \times 1/8 = 7.7 \times 10^{-7}$	7.5×10^{-10}
Silicone	2×10^{-1}	$2 \times 10^{-1} \times 0.002 \times 1/8 = 7.5 \times 10^{-5}$	7.5×10^{-10}

3. DIFFUSION FROM A SEMI-INFINITE WALL

An important case for vacuum technology is the degassing of a semi-infinite wall with an initial concentration c_1 that is exposed at $t = 0$. The boundary conditions are now:

$$P = 0 \qquad c = c_1 \qquad x > 0 \qquad t > 0$$
$$c = 0 \qquad x = 0 \qquad t > 0$$
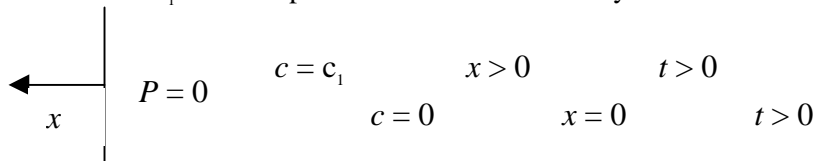
The gassing rate at time t is given by:

$$Q = c_1 < d^{-\frac{1}{2}} \left((\pi t)^{-1/2} \right).$$

When the vacuum is connected to a pump of speed S, the pressure is given by:

$$P = \frac{Q}{S} = c_1 D^{\frac{1}{2}} S^{-1} (\pi t)^{-\frac{1}{2}}.$$

The total amount of gas removed from the slab is:

$$Q_T = \int_0^t D\left(\frac{\partial c}{\partial t}\right)_{x=0} dt = 2\pi^{-\frac{1}{2}} c_1 (Dt)^{\frac{1}{2}}.$$

Note that in a log-log scale the slope is 0.5. The same amount of gas will diffuse from the atmosphere in an initially clean wall with a final concentration of c_1.

4.   DIFFUSION FROM A FINITE WALL

Another important case in vacuum engineering is the degassing from a finite wall, with uniform initial concentration c_1 and both faces are exposed to vacuum at time zero.
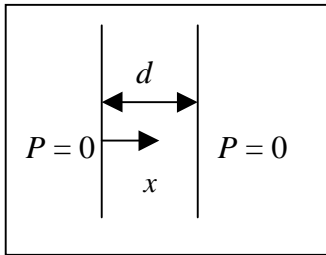
In this case the boundary conditions to solve Fick's second law are:

$$c = c_1 \qquad 0 < x < d \qquad t = 0$$
$$c = 0 \qquad x = 0, x = d \qquad t > 0$$

The instantaneous gassing rate is given by:

$$Q_{x=d} = \frac{2c_1 D}{d} \sum_{i=0}^{\infty} e^{\left(-\frac{(2i+1)\pi^2 Dt}{4d^2}\right)}$$

with

$$t_a = \frac{4d^2}{\pi^2 D}$$

which is the characteristic parameter.

According to the value of time with respect to this parameter, the instantaneous gassing rate is given by:

(1) $t > 0.5 t_a$

$$Q_{x=0,d} = \frac{2Dc_1}{d} e^{\left(-\frac{\pi^2 D}{4d^2}.t\right)}.$$

(2) $t < 0.5 t_a$

$$Q_{x=0,d} = \frac{2Dc_1}{d} \sqrt{\frac{\pi t_a}{16t}}.$$

The degree of outgassing e.g. the remaining gas in the wall with respect to the initial number of molecules, is given by the expression:

$$f = \frac{N(t)}{N_0} = \frac{8}{\pi^2}\left(e^{\frac{t}{t_a}} + \frac{e^{-9\frac{t}{t_a}}}{9} + \frac{e^{-25\frac{t}{t_a}}}{25} + \ldots\ldots\right)$$

Figure 2 shows the required time to reduce the initial outgassing rate by e for the case of $t > 0.5t_a$.

Example

Let's determine the gas diffusing from a finite nickel wall inside a vacuum system with the following parameters [4]:

Thickness: 2.10^{-3} m

Δ: 8.10^3 kg.m^{-3}
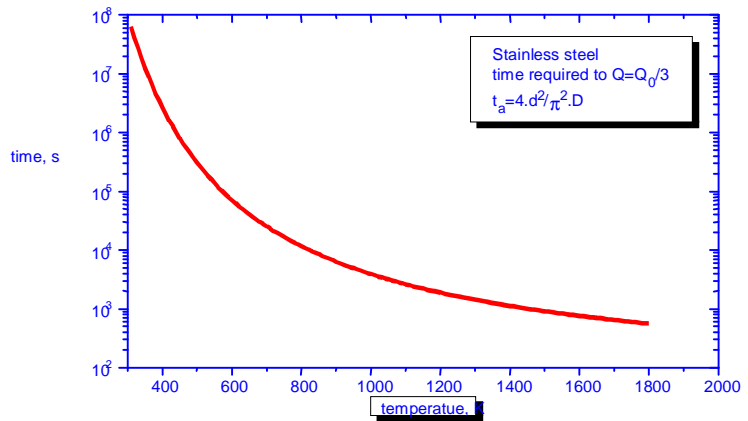
H_2 concentration: 10^{-5} (10 ppm)

Fig. 2 Time required to reduce Q_0 by a factor of e

Determination of the outgassing rates

Mass of dissolved H_2 $10^{-5} \times 8.10^3 = 8.10^{-2}$ kg.m^{-3}

Molar concentration: 8.10^{-2} kg.m^{-3}/2 kg.kmol^{-1} = 4.10^{-2} kmol.m^{-3}

Particle density number: 4.10^{-2} kmol.m^{-1}.6.10^{26} kmol^{-1} = $2.4.10^{25}$ m^{-3}

Table 3
Calculation of the diffusion rate from a nickel wall

Temp. (K)	Diffusion coefficient $D = 2.10^{-7}.e^{(-4350/T)}$ (m^2.s^{-1})	Time constant $t_a = 4d^2/BD^2$ (s)	Time to reduce concentration, $f = N/N_0$, by (s)			Gas flow at $t = 0$ $Q_0 = (2D/d)n_0$, (kg.m^{-2}.s^{-1})	Gas flow at t $Q(t) = Q_0.e^{-t/t_a}$ (kg.m^{-2}.s^{-1})
			0.1	10^{-3}	10^{-6}		
300	$1.01.10^{-13}$	$1.6.10^7$	$3.3.10^7$	$1.01.10^8$	$2.17.10^8$	$2.42.10^{15}$	$Q(t) = 2.42.10^{15}.e^{-t/t_a}$
500	$3.33.10^{-11}$	$4.87.10^4$	$1.05.10^5$	$3.26.10^5$	$6.62.10^5$	$7.99.10^{17}$	$Q(t) = 7.99.10^{17}. e^{-t/t_a}$
700	4.10^{-10}	$4.05.10^3$	$8.47.10^3$	$2.71.10^4$	$5.5.10^4$	$9.6.10^{17}$	$Q(t) = 9.6.10^{17}. e^{-t/t_a}$
1000	$2.6.10^9$	$6.23.10^2$	$1.3.10^3$	$4.17.10^3$	$8.47.10^3$	$6.24.10^{19}$	$Q(t) = 6.24.10^{19}. e^{-t/t_a}$
1300	7.10^{-9}	$2.3.10^2$	$4.81.10^2$	$1.54.10^3$	$3.13.10^3$	$1.68.10^{20}$	$Q(t) = 1.68.10^{20}. e^{-t/t_a}$

Expression of outgassing as P.V.

In practical cases, as well as in vacuum engineering, it is convenient to express the outgassing rate as P.V.

$$Q_{P.V} = P.\frac{dV}{dt} = \frac{RT}{M_{mol}}.\frac{dm}{dt} = \frac{RT}{M_{mol}}Q_m$$

Exercise: Let's apply this expression to the outgassing of a cylindrical chamber:

Concentration of H_2: $\quad c_{H2} = 8.\ 10^{-2}\ \text{kg.m}^{-3}$

Surface coverage: $\quad 2_{H2} = 10^{19}\ \text{m}^{-2}$

Areas of the inner wall: $\quad A = 5.10^{-2}\ \text{m}^2$

Temperature: $\quad T = 300\ \text{K}$

Binding energy: $\quad E = 83\ \text{kJ.mol}^{-1}.\text{K}^{-1}$

$$\frac{RT}{M_{mol}} = \frac{8.3\,\dfrac{J}{\text{mol.K}} \cdot 300\text{K}}{2\,\dfrac{\text{kg}}{\text{kmol}}} = 1.25.10^6\,\frac{J}{\text{kg}}$$

$$1.125.10^6.5.10^{-2}\,\frac{J.m^2}{\text{kg}} = 6.15.10^4\,\text{Pa.m}^3\,\frac{m^2}{\text{kg}}$$

$$Q_m = m_{H_2} v e^{-\frac{E}{RT}} = 10^{19} \cdot \frac{2}{6.10^{26}} 10^{13}\, e^{-\frac{83000\,\frac{J}{\text{mol.K}}}{8,3\frac{J}{\text{mol.K}}300\,\text{K}}} = 1.1.10^{-9}\,\frac{\text{kg}}{\text{m}^2.\text{s}}$$

$$Q_{PV} = 6.15.10^4\,\text{Pa.m}^3\,\frac{m^2}{\text{kg}} 1.1.10^{-9}\,\frac{\text{kg}}{\text{m}^2.\text{s}} = 6.8.10^{-4}\,\frac{\text{mbar.l}}{\text{s}}$$

Despite this high value it is possible to obtain ultra-high vacuum conditions in a short time because Q decreases with a time constant of 50 s. However the outgassing from diffusion has a value of:

$$Q_{PV} = 2.10^{-6}\,\frac{\text{mbar.l}}{\text{s}}$$

After only two months it will be possible to obtain ultra-high vacuum conditions because Q decreases with a very small constant time.

5.   VAPOUR PRESSURE

All materials evaporate and have a saturation pressure given by:

$$\text{Ln}P_s = A.\frac{B}{T}$$

with A and B being constants not depending on T.

The evaporation rate is given by:

$$Q_{\max} = 0.438\sigma\left(\frac{M}{T}\right)^{\frac{1}{2}} P_s \qquad \frac{\text{kg}}{\text{m}^2.\text{s}}$$

where σ is the condensation coefficient, T the surface temperature and P_s the vapour pressure at T. Table 4 shows values for the evaporation rate of some metals.

Table 4
Outgassing rates of some metals

Metal	Mol. weight	Temperature (K)	Evaporation rate, $(kg.m^{-2}.s^{-1})$
Cd	112.4	340	$2.50.10^{-11}$
Zn	65.37	390	$1.70.10^{-11}$
Ca	40.08	550	$1.18.10^{-11}$
In	114.82	760	$1.70.10^{-11}$
Ag	107.87	830	$5.70.10^{-12}$
Cu	63.54	990	$1.10.10^{-11}$
Pt	195.09	1550	$1.55.10^{-11}$
Ti	47.96	1400	$8.10.10^{-11}$
Nb	92.906	2050	$9.30.10^{-12}$
Ta	180.948	2300	$1.23.10^{-11}$
W	183.85	2400	$1.20.10^{-11}$

The materials used in ultra-high vacuum devices have vapour pressures that are negligible. However, they should be remembered when using filaments at high temperatures, such as in hot-cathode gauges and mass spectrometers.

6. ADSORPTION

All solid, as well as liquid surfaces present attraction forces normal to the surface, so molecules landing on the surface can be **adsorbed**. Adsorbed gases under certain conditions of temperature and pressure can be **desorbed**, and are the main source of gas in vacuum systems. Note that the number of molecules adsorbed is much higher than the number of molecules in the volume. Gases can be removed from the volume by the adsorption process as in sorption pumps.

The **adsorption-desorption** process is controlled by the interaction energy between the adsorbed molecule or atom with the surface atoms. According to this "**binding energy**", the adsorption can be:

Weak: physical adsorption. $E < 30$ kJ/mol

Strong: chemical adsorption. $E > 100$ kJ/mol

Figure 3 shows the potential energy curve between the surface and the adsorbate for the different kinds of adsorption [5].

6.1 Adsorption physics

6.1.1 Physisorption

When the energy of adsorption is less than 30 kJ/mol, the energy of interaction is similar to the energy between the free molecule and the molecule in the liquid phase, i.e. van der Waals forces. In this case the potential energy between the molecule and the surface is given by the Lenard-Jones potential:

$$E = E_m \left[\left(\frac{d_0}{d} \right)^{12} - \left(\frac{d_0}{d} \right)^{6} \right]$$

where E_m is the energy minima at the equilibrium distance, d_0 the equilibrium distance from the surface and D the distance from the surface. Table 5 gives some values of the physisorption energy for glass and carbon while Fig. 4 shows a typical curve of potential energy.
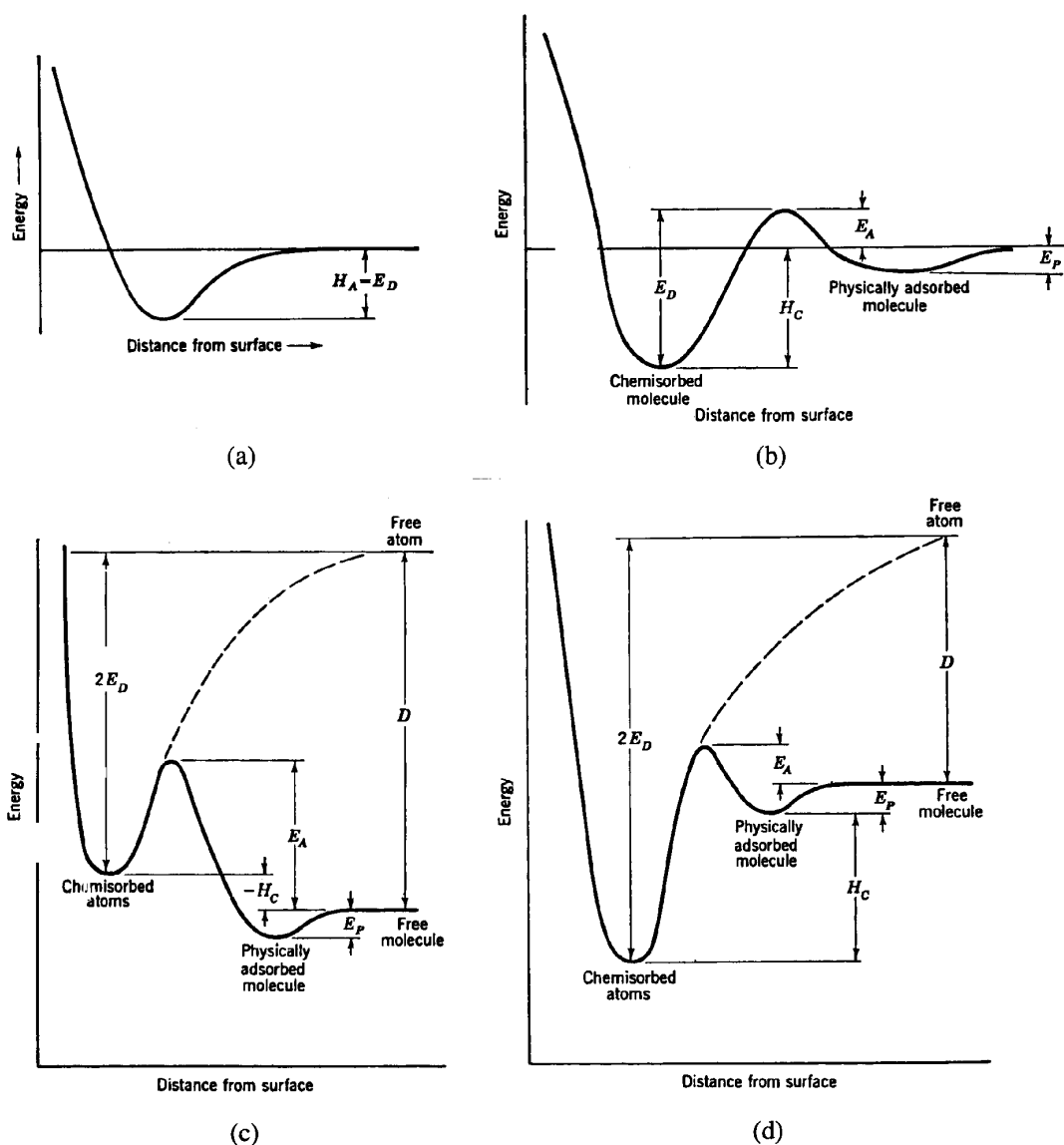
Fig. 3 Curves of potential energy surface-adsorbate. (a) is for physical adsorption. (b) Molecular chemical adsorption. (c) Endothermic dissociative chemical adsorption. (d) Exothermal dissociative chemical adsorption. H_a is the adsorption energy, E_D the desorption energy, E_p the energy for physical adsorption, E_A the activation energy for chemisorption, H_c the chemisorption energy and D the dissociation energy.

Table 5
Values of some physisorption energies

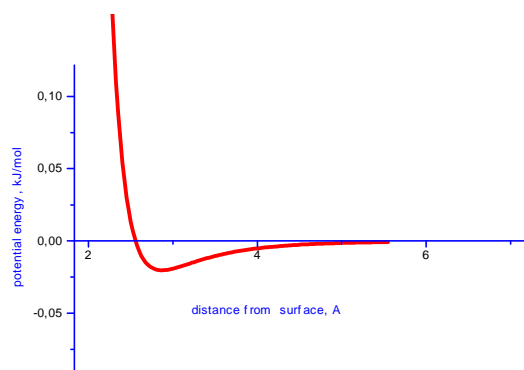| Material \ Gas	Physisorption energy (kJ/mol)		
	O_2	H_2	N_2
Glass	17.10	8.23	17.81
Carbon		78.17	15.47

Fig. 4 Curve of potential energy for physical adsorption

6.1.2 Strong chemisorption

Strong chemisorption occurs when an alkaline atom is adsorbed on a metal surface. In this case there is transference of electrons from the adsorbate to the substrate. The interaction force will be given by:

(1)   The imaginary potential when the adsorbate is at equilibrium distance d_0 from the surface.

(2)   The energy derived from the electron transference

$$E_{ads} = e(\phi - I) + \frac{e^2}{4d_0}$$

where e is the electron charge, N the work function of the metal surface, I the ionisation potential of the adsorbate and d_0 the equilibrium distance.

The equilibrium distance is given by:

$$\Delta V = 4e\pi N_s d_0$$

where N_s is the number of available sites for adsorption, and ΔV the contact potential.

6.1.3 Weak chemisorption

This case occurs when the interaction between the adsorbate and the surface is of the covalent type. The interaction energy is given by:

$$E_{ads}(A - M) = \frac{1}{2}\left[E_{dis}(A - A) + E(M - M) + \Delta s\right]$$

where $E_{ads}(A - M)$ is the energy metal-adsorbate, $E_{dis}(A - A)$ the dissociation energy of the asdsorbate A_2, $E_{dis}(M - M)$ the dissociation energy of the atom of the metal substrate (approximately the sublimation heat) and Δs the electronegativity.

The electronegativity is given by:

$$\Delta s = (\chi_M - \chi_A) \approx \mu \text{ (dipole momentum)}$$

6.1.4 Kinetics of adsorption

The number of molecules incident on a surface at a pressure P and gas temperature T is given by:

$$\frac{dn_a}{dt} = sP(2\pi mkT)^{-\frac{1}{2}} = 8.32.10^{27} sP(MT)^{-\frac{1}{2}} = k_1 sP \qquad \text{s}^{-1}\text{m}^{-2}$$

where s is the sticking coefficient, P is the pressure in mbar, M the molar mass in kg, and T the gas temperature, K.

or

$$\left(\frac{dn_a}{dt}\right) = 27.4sP\left(\frac{T}{M}\right)^{\frac{1}{2}} \text{ mbar.m}^3.\text{s}^{-1}.\text{m}^{-3}$$

The sticking coefficient is the probability for one molecule or atom to be adsorbed. Once the molecule is adsorbed it can undergo migration if the system supplies the activation energy. It is a function of the surface temperature and of surface coverage:

$$s = s_0(T)f(\theta)$$

Surface coverage, θ, is the fraction between the number of adsorbed species and the available site for adsorption. In a first approach it can be assumed that s_0 is independent of the temperature. Langmuir proposed for the dependence of s with coverage that a molecule is adsorbed when it arrives at an unoccupied site.

$$f(\theta) = 1 - \theta$$

$$s = s_0(1 - \theta)$$

and s_0 is the initial sticking coefficient at $\theta = 0$. The number of adsorbed species on a surface at a pressure P and temperature T will be the equilibrium between the rate of adsorbed molecules and the rate of desorbed molecules [6]

$$k_1 s_0 (1 - \theta)P = k_2 \theta$$

The constant of desorption rate (desorption phenomena are detailed in another chapter of these proceedings) is given by:

$$k_2 = \nu \, e^{-\frac{E}{RT}}$$

where ν is the frequency factor, 10^{13} s^{-1}, E the desorption energy, J/mol, R the gas constant, J/mol.K, and T the surface temperature, K.

The amount of adsorbed gas can be given in the form of:

$$\theta(k_2 + k_1 s_0 P) = k_1 s_0 P$$

$$\theta = \frac{k_1 s_0}{k_2} \cdot \frac{P}{1 + \frac{k_1 s_0}{k_2} P} = c\frac{P}{1 + cP}$$

which is the well-known Langmuir adsorption isotherm or the hyperbolic adsorption isotherm. Figure 5 shows a typical representation of the Langmuir isotherm and Table 6 gives some of the parameters of the adsorption kinetics.
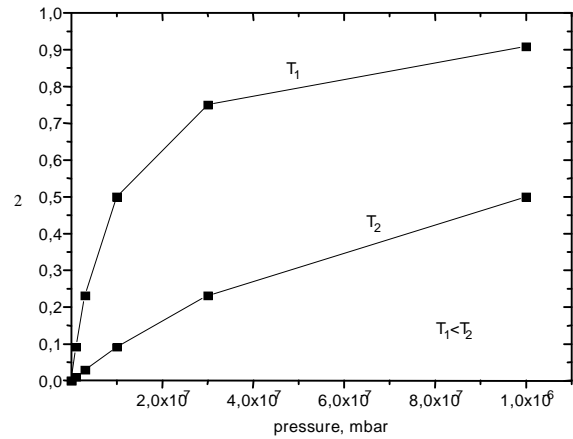

Fig. 5 Representation of the Langmuir isotherms, $T_1 < T_2$.

Table 6
Relevant parameters related to adsorption of some gas surface combinations

Gas	Surface	$T_{surface}$ K	T_{gas} (K)	s_0	$N_{maxi} \times 10^{14}$ (cm^{-2})	θ (where s_0 starts to decrease)	Activation energy for desorption (eV)
H$_2$	W(poly) [7]	300	300	0.,064	2.24	0.40	0.60
	Nb (100) [8]	90		0.23	3.20		0.03
	Ni(111) [9]	300		0.10	0.10		
CO	W(120) [10]	300		0.53	4.47	0.60	0.98
CO$_2$	W(100) [11]	300		0.85	0.42	0.20	

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