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HALF-COVERAGE TEMPERATURE AT UNIT PRESSURE AS A CHARACTERISTIC PARAMETER OF CHEMISORPTION

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The Half-Coverage Temperature at Unit Pressure is proposed as a new parameter of chemisorption, characteristic of the different types of sites of a heterogeneous surface. The temperature dependence of the adsorption equilibrium constant can be related to this new parameter.

Chemisorption is a technique widely used for the characterization of catalysts, for instance in the determination of acid-site distribution on oxides and metal dispersity in supported metals.

The models that are normally used to describe chemisorption isotherms are based on the Langmuir equation.

When dealing with catalysts having a surface with discrete inhomogeneity, the overall chemisorption isotherm can be regarded as a summation of single Langmuir isotherms, each of them relevant to a definite type of site [1-6]. The coverage degree ($\Theta = n/n_{max}$) is then related to the adsorbate pressure (p) by the following equation

$$\Theta = \sum_i \frac{f_i \, b_i \, p}{1 + b_i \, p} \tag{1}$$

where f_i and b_i are the fraction and the adsorption equilibrium constant of the i-th type of site, respectively. The total number of molecules adsorbed at a given p is the sum of the number of molecules adsorbed on each type of site:

$$n=\sum_i n_i$$

The parameters obtainable by fitting isothermal chemisorption data on the basis of Eq. 1 are b_i and $n_{i,max}=f_i\ n_{max}$.

When chemisorption data are collected at different temperatures ranging over an interval in which the surface does not undergo modifications, the constants b_i can be evaluated as a function of temperature (T), usually by the following equation

$$\ln b_i=-\frac{\Delta_a H_i}{R\ T}+\ln b_{o,i}$$

where $\Delta_a H_i$ is the enthalpy of adsorption on sites of type i.

In the present note, the possibility is taken into account to express the dependence of b_i on T through $\Delta_a H_i$ and a new parameter, the Half-Coverage Temperature at Unit Pressure, $T°_{1/2,i}$. The latter corresponds to the temperature at which the sites of the i-th type are half-covered by an adsorbate with partial pressure in the gas-phase equal to one.

The theoretical procedure for obtaining this parameter for the simple case of a homogeneous surface is shown below. The practical advantages of utilizing this parameter are also discussed.

Theoretical considerations. For a gas in equilibrium with a homogeneous surface on which it is chemisorbed without either dissociation or intermolecular interaction among adsorbed molecules, at a given T, the relationship between Θ and p follows the Langmuir isotherm:

$$\Theta=\frac{b\ p}{1+b\ p} \qquad (2)$$

For an adsorption equilibrium with T as a variable, the dependence of the adsorption constant (b) on T has to be considered:

$$\left(\frac{\partial \ln b}{\partial T}\right)_p = \frac{\Delta_a H}{R\ T^2} \qquad (3)$$

When the temperature range is small enough, $\Delta_a H$ may be taken as a constant and the integration of Eq. 3 gives

$$\ln b = -\frac{\Delta_a H}{R\ T} + \ln b_o \qquad (4)$$

The integration constant, $\ln b_o$, corresponds to

$$\ln b_o = \lim_{T \to \infty} \ln b \qquad (5)$$

If the temperature range is wider, one must also introduce the dependence of $\Delta_a H$ on T:

$$\left(\frac{\partial \Delta_a H}{\partial T}\right)_p = \Delta_a C_p \qquad (6)$$

where $\Delta_a C_p$ is the heat capacity of adsorption.

Unless large intervals of temperature are involved, $\Delta_a C_p$ can be considered as a constant and the integration of Eq. 6 gives

$$\Delta_a H = \Delta_a H_o + \Delta_a C_p T$$

where $\Delta_a H_o$ is simply an integration constant. If this is the case, the integration of Eq. 3 gives

$$\ln b = -\frac{\Delta_a H_o}{R\ T} + \frac{\Delta_a C_p}{R} \ln T + \ln b_o \qquad (7)$$

The evaluation of the integration constant $\ln b_o$ is not as easy as in the previous case. In fact, it is no longer possible to obtain it as the limit of ln b when T $\longrightarrow \infty$, because

$$\lim_{T \to \infty} \left(- \frac{\Delta_a H_o}{R\ T} + \frac{\Delta_a C_p}{R} \ln T \right) = \infty$$

On the other hand, the integration constant can neither be obtained as the limit of ln b when T $\longrightarrow$ 0, as

$$\lim_{T \to \infty} \left(- \frac{\Delta_a H_o}{R\ T} + \frac{\Delta_a C_p}{R} \ln T \right) = - \infty$$

A way to evaluate the integration constant of Eq. 7 is to define a characteristic temperature, T*, at which b becomes unity. Thus

$$\ln b_o = \frac{\Delta_a H_o}{R\ T^*} - \frac{\Delta_a C_p}{R} \ln T^* \qquad (8)$$

When b is unity, on the basis of Eq. 2, $\Theta = p/(1+p)$ and, at unit pressure, $\Theta = 1/2$. This means that T* corresponds to the temperature at which the surface is half-covered when p=1. As a consequence, the Half-Coverage Temperature at Unit Pressure $T°_{1/2}$ can be defined to be equal to T*.

By introducing $T°_{1/2}$, Eq. 8 can be rewritten as:

$$\ln b_o = \frac{\Delta_a H_o}{R\ T°_{1/2}} - \frac{\Delta_a C_p}{R} \cdot \ln T°_{1/2} \qquad (9)$$

Obviously, the numerical value of $T°_{1/2}$ depends on the units in which the pressure is expressed (Fig. 1).

If the heat capacity cannot be considered as a constant, that is:

$$\Delta_a C_p = \alpha + \beta\ T + \gamma\ T^2 + \ldots\ldots$$

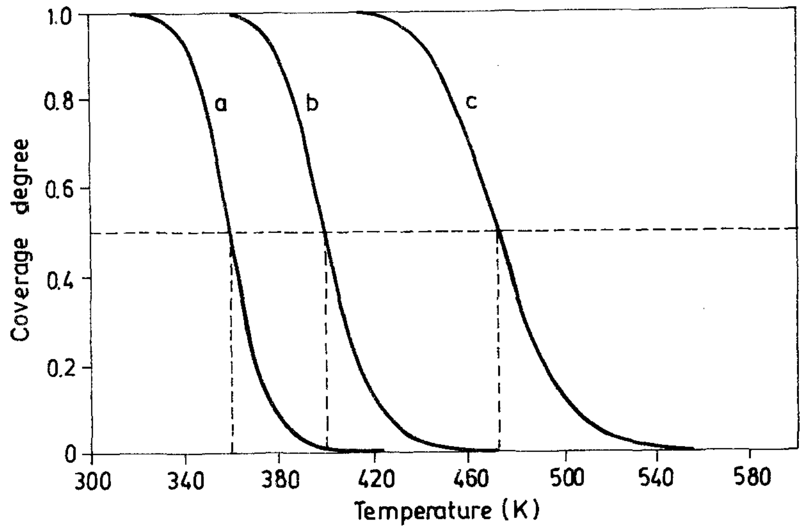

Fig. 1. Simulated adsorption isobars as a function of coverage at 1 Pascal (a), 1 Torr (b), and 1 Bar (c) (ΔH_o=-140 kJ/mol, ΔC_p=-10 J $mol^{-1}K^{-1}$). $T°_{1/2}$= 359 (a), 400 (b), and 472 K (c)

following an argument analogous to the previous, Eqs 7 and 9 have to be rewritten, respectively, as:

$$\ln b = -\frac{\Delta_a H_o}{R\ T} + \frac{\alpha}{R} \ln T + \frac{\beta}{2\ R}\ T + \frac{\gamma}{6\ R}\ T^2 + \ldots \ln b_o$$

$$\ln b_o = \frac{\Delta_a H_o}{R\ T°_{1/2}} - \frac{\alpha}{R} \ln T°_{1/2} - \frac{\beta}{2\ R} T°_{1/2} - \frac{\gamma}{6\ R} (T°_{1/2})^2 - .. \quad (10)$$

On the other hand, when $\Delta_a H$ is a constant and Eq. 4 holds, for $T=T°_{1/2}$ one obtains:

$$0 = -\frac{\Delta_o H}{R\ T°_{1/2}} + \ln b_o$$

from which it follows, on the basis of Eq. 5 that

$$\ln b_o = \lim_{T\to\infty} \ln b = \frac{\Delta_a H}{R\,T°_{1/2}} \qquad (11)$$

Equations 11, 9, and 10 relate b_o to $T°_{1/2}$ in the three different cases taken into account, respectively: (i) $\Delta_a H$ is independent of temperature; (ii) $\Delta_a H$ is dependent on temperature but $\Delta_a C_p$ is not; (iii) $\Delta_a C_p$ and, consequently, $\Delta_a H$ are dependent on temperature.

Practical considerations. The parameters that can be obtained by applying the Langmuir equation to isothermal experimental data of chemisorption on a homogeneous surface are n_{max} and b. When experimental data are obtained at different temperatures, instead of, b one can evaluate the parameters which permit the expression of b as a function of T, for instance: $\Delta_a H_o$, $\Delta_a C_p$, and b_o.

When a catalyst with a heterogeneous surface is taken into account, the above parameters have to be determined for each type of site. In this case, one needs a sufficiently large number of experimental data. The desired parameters ($\Delta_a H_{o,i}$, $\Delta_a C_{p,i}$, and $b_{o,i}$) cannot be obtained employing the usual linearized Langmuir equation, but have to be evaluated by optimization through procedures of fitting of the experimental data.

As concerns the parameter b_o of Eq. 4, it could be theoretically evaluated by a statistical thermodynamic approach employing the partition functions of the adsorbate in the gas phase and in the adsorbed state [7, 8]. However, when heterogeneous surfaces are involved, the evaluation of the various $b_{o,i}$ is not easy. A great number of rotation and vibration data relevant to each adsorbed molecule on each type of site, as well as the adsorption energy of each site, are required. Such a huge quantity of data is often not available.

From a mathematical point of view, b_o can be seen as a mere integration constant independent of temperature in the temperature interval considered, as in our approach. Equations 9, 10, and 11 permit calculating b_o, if $T°_{1/2}$ and $\Delta_a H$, with its dependence on temperature for Eqs 9 and 10 are known. The b_o values reported in Table 1 have been generated by Eq. 9, employing values of $\Delta_a H_o$ in the range of (-250) - (-100) kJ/mol, typical for chemisorption, $T°_{1/2}$ values in the range of 400 - 600 K, and values of $\Delta_a C_p$ of -10, 0, and 10 J mol^{-1} K^{-1}. The range of $\Delta_a C_p$ employed for the computation has been taken sufficiently large to cover the whole field of the real values. Table 1 shows the extreme large interval of the obtainable b_o values: differences up to more than 20 orders of magnitude among the values can be noticed.

Due to the wide range of the possible values of b_o, and particularly of the different $b_{o,i}$ when different types of site are present, the investigator who is handling the data is somewhat disoriented, because little of his experience can help him in the evaluation of the soundness of these parameters obtained by optimization.

Table 1

Values of b_o calculated by equation 9

$T^o_{1/2}$ (K):		400	500	600
ΔH_o (kJ/mol)	ΔC_p (J/mol K)		b_o ($Torr^{-1}$)	
-250	-10	$3.04\text{x}10^{-30}$	$1.35\text{x}10^{-23}$	$3.78\text{x}10^{-19}$
-200		$1.03\text{x}10^{-23}$	$2.25\text{x}10^{-18}$	$8.51\text{x}10^{-15}$
-150		$3.48\text{x}10^{-17}$	$3.77\text{x}10^{-13}$	$1.92\text{x}10^{-10}$
-100		$1.18\text{x}10^{-10}$	$6.30\text{x}10^{-08}$	$4.32\text{x}10^{-06}$
-250	0	$2.26\text{x}10^{-33}$	$7.64\text{x}10^{-27}$	$1.72\text{x}10^{-22}$
-200		$7.64\text{x}10^{-27}$	$1.28\text{x}10^{-21}$	$3.88\text{x}10^{-18}$
-150		$2.58\text{x}10^{-20}$	$2.14\text{x}10^{-16}$	$8.74\text{x}10^{-14}$
-100		$8.74\text{x}10^{-14}$	$3.57\text{x}10^{-11}$	$1.97\text{x}10^{-09}$
-250	10	$1.68\text{x}10^{-36}$	$4.33\text{x}10^{-30}$	$7.84\text{x}10^{-26}$
-200		$5.67\text{x}10^{-30}$	$7.25\text{x}10^{-25}$	$1.77\text{x}10^{-21}$
-150		$1.92\text{x}10^{-23}$	$1.21\text{x}10^{-19}$	$3.98\text{x}10^{-17}$
-100		$6.49\text{x}10^{-17}$	$2.03\text{x}10^{-14}$	$8.97\text{x}10^{-13}$

It could be more useful to optimize the new parameter $T°_{1/2}$ instead of b_o, thus avoiding the above discussed difficulties in judging the soundness of b_o. The two parameters are correlated by equation 9 (or 10 or 11) and can be obtained one from the other. $T°_{1/2}$ should be more familiar than b_o, due to its simple physical meaning. The estimation of its validity should be easier. For instance, when a set of isotherms of chemisorption on a homogeneous surface has been collected at different temperatures, one could easily estimate where $T°_{1/2}$ has to be located as shown in Fig. 2.

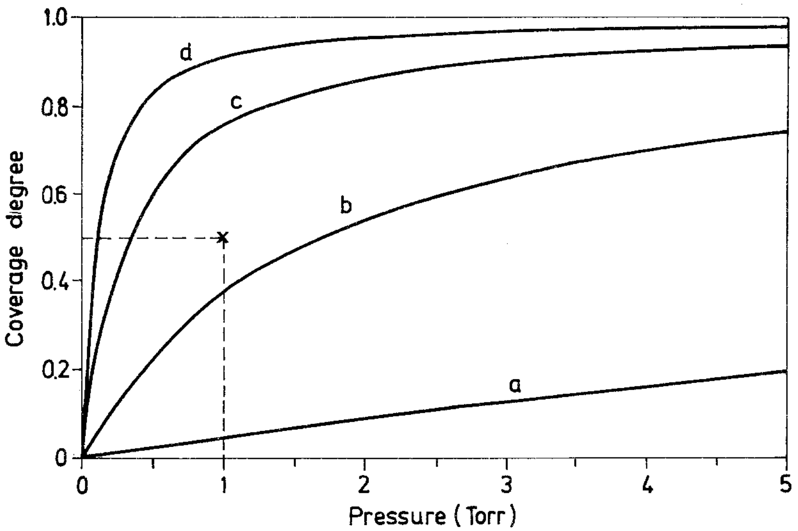

Fig. 2. Simulated adsorption isotherms as a function of coverage at different temperatures: 430 (a), 405 (b), 390 (c), and 380 K (d) (ΔH_o=-140 kJ/mol, ΔC_p=-10 J mol^{-1} K^{-1}). The isotherm at $T°_{1/2}$ (400 K) passes through the indicated point (X)

When heterogeneous surfaces are taken into account, it will be possible to obtain a $T^\circ_{1/2,i}$ for each site of type i.

This new parameter has been successfully utilized in the treatment of experimental data of chemisorption of ammonia in the study of acid site distribution of metal oxide catalysts [9].

To sum up, the Half-Coverage Temperature at Unit Pressure, can be considered as a characteristic parameter of a homogeneous surface or of a single type of site of a heterogeneous surface. The definition and existence of $T^\circ_{1/2}$ is independent of the kind of model isotherm employed, either Langmuir or some other. Obviously, the relation between this parameter and the other adsorption parameters will be different depending on the model isotherm, and will have to be determined in each different case.

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