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THERMODYNAMICS OF ADSORPTION OF MIXED METALLIC ELEMENTS
ON GRAPHITE AT HIGH TEMPERATURE

by

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INTRODUCTION

In studies of the behavior of cesium⁽¹⁾ and barium⁽²⁾ adsorbed on graphite it has been demonstrated that the experimental data can be represented by a Freundlich-type isotherm. Halsey⁽³⁾ has given a theoretical derivation of the Freundlich isotherm essentially as follows: He assumes adsorption on sites of energy $X^\dagger$ to be unaffected by adsorption on neighboring sites. When the gas phase and an adsorbed layer are in equilibrium, the rate of vaporization of a species equals its rate of condensation. The rate of vaporization is proportional to the surface coverage $\theta(X)$, while the rate of condensation is proportional to the pressure p of the condensing species times the fraction of the surface uncovered or

$$\theta(X) = b(X)p[1 - \theta(X)] \quad (1)$$

Solving this equation for $\theta(X)$ gives the Langmuir isotherm

$$\theta(X) = \frac{b(X)p}{1 + b(X)p} \quad (2)$$

If one now considers the fractional number of sites of energy $N(X)$ such that

$$\int_0^\infty N(X) dX = 1 \quad (3)$$

then the total fractional coverage of all available sites is

$$\theta = \int_0^\infty \theta(X) N(X) dX \quad (4)$$

The main premise of the Freundlich isotherm is that a number of sites of energy X are distributed exponentially with the site energy, such that the lowest energy sites approach zero energy. (The vaporization energy at monolayer loading is assumed to be zero.)

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[†]Strictly $-X$ is the enthalpy of adsorption relative to the monolayer state (where $X = 0$).

$$N(X) = A \exp(-BX) \quad (5)$$

Then, according to Eq. 3, A equals B, and, by definition, A equals $1/X_m$. The Freundlich isotherm derivation continues according to a combination of Eqs. 2, 4, and 5:

$$\theta = \int_0^\infty \frac{b(X)p \exp(-X/X_m) dX}{[1 + b(X)p] X_m} \quad (6)$$

It is now necessary to define $b(X)$. This term in the Langmuir derivation is a thermodynamic term involving an adsorption enthalpy $-X$ and an adsorption entropy $-\Delta S(X)$:

$$b(X) = \exp(X/RT) \exp[-\Delta S(X)/R] \quad (7)$$

Halsey takes $\Delta S(X)$ as a linear function of adsorption energy (compensated); that is,

$$\Delta S(X) = \Delta S_o + rX \quad (8)$$

and

$$b(X) = \exp[X(1 - rT)/RT] \exp(-\Delta S_o) = \frac{\exp[X(1 - rT)/RT]}{p_o} \quad (9)$$

Substituting $b(X)$ according to Eq. 9 into Eq. 6 gives

$$\theta = \frac{p}{X_m p_o} \int_0^\infty \frac{\exp[X(1 - rT)/RT] \exp(-X/X_m) dX}{(1 + p/p_o \exp[X(1 - rT)/RT])} \quad (10)$$

Halsey integrates essentially this equation between $-\infty$ and ∞ for X and obtains Eq. 11 for the description of a Freundlich isotherm:

$$\theta = (p/p_o)^{RT/X_m(1 - rT)}, \quad (11)$$

which is applicable to a single species sorbed on graphite. Halsey used the limits of $-\infty$ and ∞ , rather than 0 and ∞ , in order to facilitate integration.

This is the form of the Freundlich equation used here to describe sorption behavior of metals on graphite when the terms p_o and θ are modified to include the vaporization equation for the metal. The quantity $X_m(1 - rT)/RT$ has been simplified to $A + B/T$, giving

$$\log (P/P_o) = (A + B/T) \log (C/C_o) \quad (12)$$

Mathematically, isothermal plots of $\log P$ versus $\log C$ are represented by lines intersecting at $\log P_o$, $\log C_o$ and spaced according to $(A + B/T)$, as shown in Fig. 1. Experimentally, Freundlich adsorption behavior is considered to be indicated by linear dependence of $\log P$ on

$\log C$ and linear dependence of heat of sorption on $\log C$, the slope of the former line being temperature dependent.

The general equation for describing Freundlich relationships is Eq. 12. As stated, the isotherms representing this equation converge at C_o ; it should be noted that C_o does not represent the monolayer concentration. To obtain a set of lines that converge at the Freundlich monolayer concentration, one can consider activities of the adsorbed species, rather than vapor pressures. The dependence of activity a on concentration is obtained by subtracting the vapor pressure equation for the pure substance, $\log P' = A' + B'/T$, from Eq. 12. This results in

$$\log a/a_o = (A + B/T) \log(C/C_m) , \quad (13)$$

where C_m is the Freundlich monolayer concentration, and A and B are the same constants presented in Eq. 12. By definition, the activity ratio a/a_o at a monolayer is unity.

EXPERIMENTAL

Studies of the vaporization of strontium and barium (M) from TS-688 graphite and barium from HLM-85 graphite have been made using the Knudsen cell mass spectrometric method. The experimental apparatus is shown in Fig. 2. A graphite sample (ground to 37 to 74 μ), which had been degassed at 2000°C, was impregnated with $M(NO_3)_2$ to the desired concentration level by evaporating a mixture of the graphite and metal nitrate solution to dryness. A weighed portion of the impregnated graphite was placed in a tantalum Knudsen cell (having an orifice 0.33 mm in diameter and 1.6 mm long) and, in an inert atmosphere, the cell was closed, except for the orifice, by welding. This cell was installed in the mass spectrometer and heated to convert the $M(NO_3)_2$ to sorbed metal. After the conversion process, the temperature of the cell was further increased until metal vapors were observed to be effusing from the cell in appreciable quantities. This metal beam was monitored by ionizing a portion of it in an ionization chamber and measuring the intensity of the subsequently mass analyzed metal ion beam. The intensities of the metal beam were measured as a function of time and temperature.

After the effusion process was halted, the metal content of the

remaining graphite was determined by activation analysis. This value was compared with the initial amount of metal present. The difference, $\int_c (dg/dt) dt$ was then related to the time integrated ion signal from the mass spectrometer according to the Knudsen equation

$$\int_c \frac{dg}{dt} dt = \frac{AM^{1/2}K}{0.02256} \int_c IT^{1/2} dt , \quad (14)$$

where

$$KIT = p . \quad (15)$$

In Eqs. 14 and 15, I is the ion signal, T is the temperature in $^{\circ}\text{K}$, p is the pressure in atmospheres, M is the gram molecular weight of the effusing species, A is the effective orifice area in cm^2 , dg/dt represents a rate of loss in g/sec, and K is a constant depending on the mass spectrometric sensitivity. The value of K is determined from Eq. 14, and a pressure for any signal can be determined from Eq. 15. The quantity of metal in the cell at any time t is obtained by numerically integrating Eq. 14 between limits. Sorption of barium on the walls of the tantalum cell during this type of experiment has been found to be relatively unimportant. However, strontium has been found to be more strongly wall-sorbed, and the effect of this sorption needs to be considered since this phenomenon affects the apparent dg/dt.

Application of the thermodynamic relation $-(d \ln p)/d(1/T) = \Delta H_v/R$ to Eq. 12 yields

$$-4.575 B \log(C/C_o) = \Delta H_v , \quad (16)$$

where ΔH_v is the heat of vaporization in kcal/mole. This equation is used in the analysis of the data.

RESULTS

Data obtained from the study of the barium/HLM-85 graphite system ($10 \text{ m}^2/\text{g}$) are shown in Figs. 3 and 4. Figure 3 is a plot of $\log P$ versus $\log C$ at 1829°K . The linear dependence observed satisfies one requirement of the Freundlich isotherm. Figure 4 is a plot of the heat of vaporization of barium (determined from $\log P$ versus $1/T$ data at essentially constant C) versus the logarithm of the concentration. Linear behavior with the heat increasing as the concentration decreases fulfills the other theoretical requirement.

Part of the Freundlich description involves the concept of a monolayer quantity. Although this quantity is in reality an ill-defined physical entity,

adsorption models generally are dependent on it. In this work attempts have been made to describe a monolayer in three ways: (1) a geometrical correlation of nitrogen BET surface areas with metal monolayers using atomic radii, (2) the assumption that a monolayer exists when the vapor pressure of the metal is the same as that of some thermodynamically carbon-compatible metal-containing phase, and (3) the assumption that a monolayer exists when the heat of vaporization of the metal is the same as that of the phase described in (2). For Ba and Sr in this type of study, this phase has been chosen as $MC_2(s)$.

Flowers and Rauh⁽⁴⁾ have reported vapor pressure data for both BaC_2 and SrC_2 . Using their data and surface area measurements, one can calculate the monolayer concentrations for each of the three methods described above. Values for Ba on HLM-85 graphite and Sr and Ba on TS-688 graphite are shown in Table 1.

Table 1
MONOLAYER CONCENTRATION

Element (M)	Monolayer Concentration (mg M/g C)		
	Pressure Method (at 1800°K)	Heat of Vaporization Method	Geometry (BET) Method
Ba (HLM-85)	10.2	4.0	14
Sr (TS-688)	5.1	2.5	5.3
Ba (TS-688)	3.0	1.7	8.2

The geometry calculations were made assuming a 4.35 Å diameter for barium and a 4.31 Å diameter for strontium according to Barrett⁽⁵⁾ at 20°C. The agreement among these methods is striking, particularly for strontium.

These studies have yielded the following Freundlich equations for Ba and for Sr in TS-688 graphite and for Ba in HLM-85 graphite, respectively:

$$\log(P_{Ba}/1.95) = (-1.304 + 7553/T) \log(C/0.070) \quad (17)$$

$$\log(P_{Sr}/10^{3.28}) = (-0.1074 + 4444/T) \log(C/1.17) \quad (18)$$

and

$$\log(P_{Ba}/0.66) = (-1.252 + 6534/T) \log(C/0.30) \quad (19)$$

where P is in atmospheres, T is in °K, and C is in g metal/g graphite (graphite surface area = 5.87 m²/g C TS-688 and 10 m²/g C HLM-85) using a 4.56 Å diameter for N₂ at 78°K.

MIXED SPECIES BEHAVIOR

THEORETICAL

The previous studies described the behavior of a single sorbed species only. However, several metallic products may be sorbed simultaneously. Thus, appropriate equations to describe cosorption phenomena are needed. Glueckauf⁽⁶⁾ presented the first theoretical treatment of binary element Freundlich adsorption. The mixed isotherm description presented here is more inclusive and represents all concentration levels for multielement Freundlich adsorption. The mixed isotherm description parallels the single species description. First, the Langmuir description of equilibrium conditions for the i^{th} element can be written as

$$\theta_i(X_i) = b_i(X_i) p_i \left[1 - \sum_{j=1}^h \theta_j(X_j) \right] \quad (20)$$

for energy X_j associated with the j^{th} element. If one sums this equation over all the elements, one obtains

$$\sum_{j=1}^h \theta_j(X_j) = \left[1 - \sum_{j=1}^h \theta_j(X_j) \right] \sum_{j=1}^h p_j b_j(X_j) \quad (21)$$

Solving Eq. 21 for $\sum_{j=1}^h \theta_j(X_j)$ gives

$$\sum_{j=1}^h \theta_j(X_j) = \frac{\sum_{j=1}^h p_j b_j(X_j)}{1 + \sum_{j=1}^h p_j b_j(X_j)} \quad (22)$$

Substitution of Eq. 22 into Eq. 20 gives

$$\theta_i(X_i) = \frac{b_i(X_i) p_i}{1 + \sum_{j=1}^h p_j b_j(X_j)} \quad (23)$$

which is the mixed system counterpart of the Langmuir isotherm (Eq. 2).

Equations 3, 4, and 5 have exact counterparts in the mixed system derivation using the mixed system components. The counterpart of Eq. 6 then is

$$\theta_i = \int_0^\infty \frac{b_i(X_i) p_i \exp(-X_i/X_{mi}) dX_i}{\left[1 + \sum_{j=1}^h b_j(X_j) p_j \right] X_{mi}} \quad (24)$$

In the description of $b_i(X_i)$, Eqs. 7, 8, and 9 also have exact counterparts, and substitution of the counterpart of Eq. 9 into Eq. 24 leads to the following integral equation:

$$\theta_i = \frac{p_i}{X_{mi} p_{oi}} \int_0^\infty \frac{\exp[X_i(1 - r_i T)/RT] \exp(-X_i/X_{mi}) dX_i}{\left(1 + \sum_{j=1}^h \frac{p_j}{p_{oj}} \exp[X_j(1 - r_j T)/RT]\right)} \quad (25)$$

This equation may be solved numerically for each θ_i , given values of p_i , single species Freundlich equations, and X_j proportional to X_i .

RESULTS

In one experiment, 0.4283 g TS-688 graphite, having a BET (nitrogen adsorption) surface area of $5.87 \text{ m}^2/\text{g C}$, was loaded with 8.30 mg Sr/g C and 4.11 mg Ba/g C (both elements present as nitrates). After decomposition of the nitrates, the Ba and Sr ion intensities were followed throughout the experiment as a function of time and temperature.

The results of this experiment are shown in Fig. 5, a plot of log concentration versus log pressure, and in Fig. 6, a plot of log concentration versus heat of vaporization. In these figures, isochronal equilibrium data are shown using alphabetical designations. In the initial phase of this experiment, the Sr pressures decreased, as shown in points A through K; correspondingly, a slight increase was observed in the barium pressure. Immediately after point K, a change in behavior was noted; the pressures of both elements decreased sharply. The strontium, which at this point was loaded to about 10% of the barium loading, showed a rapid drop. Barium, however, exhibited a behavior similar to that previously observed in studies of the barium-graphite systems. The rapid drop in Sr pressure continued from points L through P before reaching a region in which the pressure decreased much more slowly with changes in concentration, i. e., points Q through Y.

In order to better understand the experimental data, a form of the mixed element Freundlich adsorption solution (Eq. 25) has been programmed to provide calculated loadings of adsorbed elements from their partial pressures, single element Freundlich adsorption data, X_j proportional to X_i , and monolayer coverages for these elements. Using this program, together with the Freundlich data for Ba and Sr and monolayer pressures of these elements as deduced from carbide vapor pressures,⁽⁴⁾ calculations of loading versus vapor pressure have been made at a constant temperature. The results of

these calculations are presented in Figs. 7 and 8. Figure 7 shows pressure-loading relationships for Ba at constant Sr pressures, and Fig. 8 shows pressure-loading relationships for Sr at constant Ba pressures.

The two types of asymptotes demonstrated in these figures are interesting. If the contaminating element is of very low loading, $\theta_1 \gg \theta_2$, the pressure-loading curve (P_1, θ_1) approaches Freundlich behavior for the single element. If the contaminating element is of very high loading, $\theta_2 \gg \theta_1$, then the pressure-loading curves are families of Langmuir-type adsorption isotherms depending on the exact contaminant loading. This Langmuir-type behavior has been predicted by Glueckauf⁽⁶⁾ for mixed systems.

While some of the features of the calculated plots can be recognized in the experimental data, the experimental plots may not at present be totally resolved in terms of the theory. A continuation of these studies is planned with the purpose of obtaining a better understanding of the sorption phenomena.

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Fig. 1. Basic Freundlich adsorption isotherms

Fig. 2. Tantalum Knudsen cell and furnace

Fig. 3. Vapor pressure of barium adsorbed on HLM-85 graphite

Fig. 4. Concentration dependence of heat of vaporization of barium adsorbed on HLM-85 graphite

Fig. 5. Barium and strontium pressure as a function of concentration of metals in TS-688 graphite. (Surface area = $5.87 \text{ m}^2/\text{g C}$, $T = 1800^\circ\text{K}$)

Fig. 6. Heat of vaporization versus loading of barium and strontium for TS-688 graphite

Fig. 7. Calculated loading versus vapor pressure for barium in TS-688 graphite (at constant P_{Sr}), $T = 1800^\circ\text{K}$

Fig. 8. Calculated loading versus vapor pressure for strontium in TS-688 graphite (at constant P_{Ba}), $T = 1800^\circ\text{K}$