Origin of Surface Potentials in Physical Adsorption

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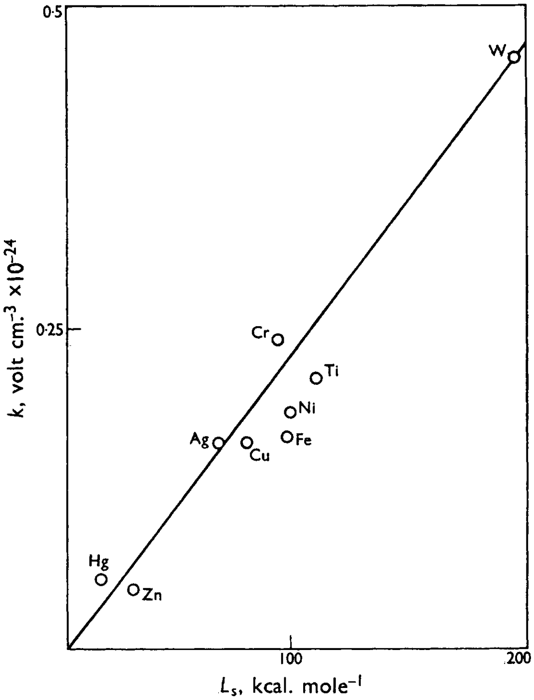
MIGNOLET[1] originally attributed the positive surface potentials of physically adsorbed gases on metals to polarisation of the adsorbate by the external field, but later he suggested[2] that charge-transfer no-bond interaction was more feasible. On the other hand, de Boer[3] has maintained that polarisation is the important factor. Gundry and Tompkins[4] showed that polarisation theory was quantitatively adequate for inert gas adsorbates; a linear correlation between surface potential and polarisability was evident. However, they also showed that the surface potentials could be rationalized in terms of charge-transfer theory, and concluded that it was difficult to decide which of the two theories was more applicable. In this Communication, an analysis of surface potential results is shown to favour the classical polarisation approach and to provide further information about the field strength at a metal surface.

With the majority of metal–gas systems in physical adsorption, the surface potential (S.P.) is related to the polarisability, α, of the adsorbate by the empirical equation,

$$\text{S.P.} \sim k\alpha \qquad (1)$$

where k is a constant for a given metal. In the Table, values of $k\alpha$ are compared with the experimental values of S.P. The latter are those given by Mignolet[2] unless otherwise stated. The values of k are also shown; these were determined from plots of S.P. against α for metals for which data for more than one gas were available. The systems which show marked deviations from equation (1) are grouped together at the lower end of the Table.



FIGURE

S.P. correlation constant k *as a function of the heat of sublimation,* L_S, *of the metal.*

The form of equation (1) suggests that k is related to the surface field strength. Furthermore, k is shown (Figure) to be an approximate linear

TABLE

Correlation between surface potential and polarisability

	$\alpha \times 10^{24}$ (cm.^{3})	$k \times 10^{-24}$ (volt cm.$^{-3}$	$k\alpha$ (volt)	S.P. (volt)
Hg–CH_4	2·60	0·0556	0·14	+0·16[a]
Hg–C_2H_2	3·33	0·0556	0·185	+0·21
Hg–Xe	4·0	0·0556	0·22	+0·23
Hg–C_2H_4	4·26	0·0556	0·235	+0·27
Hg–C_2H_6	4·47	0·0556	0·245	+0·23
Zn–CO	1·93	0·0474	0·09	+0·075[b]
Zn–Xe	4·0	0·0474	0·19	+0·21
Cu–CO	1·93	0·160	0·305	+0·30[c]
Cu–Xe	4·0	0·160	0·64	+0·67
Cu–C_2H_6	4·47	0·160	0·715	+0·69
Ni–Xe	4·0	0·184	0·74	+0·85
Ni–C_2H_4	4·26	0·184	0·79	+0·83[d]
Ni–C_2H_6	4·47	0·184	0·825	+0·77
W–Ne	0·39	0·478	0·185	+0·15[e]
W–Ar	1·63	0·478	0·78	+0·80[e]
W–Kr	2·46	0·478	1·18	+1·18[f]
(WO)[g]–O_2	1·56	0·0682	0·105	+0·08
(WO)[g]–Xe	4·0	0·0682	0·275	+0·30
(WO)[h]–O_2	1·56	0·0275	0·043	+0·035
(WO)[h]–Xe	4·0	0·0275	0·11	+0·12
Hg–O_2	1·56	0·0556	0·08	+0·03[a]
Cu–N_2	1·73	0·160	0·28	+0·45[a]
Cu–CH_4	2·60	0·160	0·415	+0·14[a]
Cu–C_2H_4	4·26	0·160	0·685	+1·2
Ni–N_2	1·73	0·184	0·32	+0·21[d]
W–Xe	4·0	0·478	1·91	+1·40[e]

[a] Incomplete coverage.

[b] Quoted by G. C. Bond, "Catalysis by Metals", Academic Press, London and New York, 1962, p. 89.

[c] Quoted by R. V. Culver and F. C. Tompkins, *Adv. Catalysis*, 1959, **11**, 104.

[d] Quoted by R. V. Culver and F. C. Tompkins, *Adv. Catalysis*, 1959, **11**, 97.

[e] R. Gomer, *J. Chem. Phys.*, 1958, **29**, 443.

[f] G. Ehrlich and F. G. Hudda, *J. Chem. Phys.*, 1959, **30**, 493.

[g] Incomplete film of pre-chemisorbed O_2.

[h] Near-complete film of pre-chemisorbed O_2.

function of the heat of sublimation,[5] L_S (kcal. mole^{-1}) of the metal according to the equation,

$$k \sim 2{\cdot}25\, L_S \times 10^{21} \qquad (2)$$

The points shown for Fe, Cr, Ti, and Ag represent the values of S.P./α for the systems[2] Fe–Xe (0·66), Cr–Xe (0·95), Ti–Xe (0·84) and the system (ref. c, Table footnote) Ag–CO (0·31); S.P. values are in parentheses.

At monolayer coverage ($\theta = 1$), the surface potential can be expressed as,

$$\text{S.P.} = 4\pi n_S m = 4\pi n_S F\alpha \qquad (3)$$

where n_S is the average number of surface sites per cm.^{2}, m is the surface dipole moment, and F is the average strength of the polarising field acting on the adsorbate. Therefore, from equations (1)—(3),

$$F \sim 1{\cdot}8\, L_S/n_S \times 10^{20} \text{ volt cm.}^{-1} \qquad (4)$$

where L_S and n_S are expressed in kcal.mole^{-1} and cm.$^{-2}$, respectively. Values of F calculated from equation (4) using data for n_S given by Brennan *et al.*,[6] are about 10^7 volt cm.$^{-1}$.

Equation (4) explains the parallelism between the surface potentials and the cohesion of the substrate, noted by Mignolet.[2] Qualitatively, it is reasonable that the surface field strength should depend on the surface site density and the electronic structure of the metal. The heat of sublimation is dependent on lattice constants and electronic structure, hence it is indirectly related to surface site density.

Mignolet[2] regarded the surface potentials for the transition metals as being high because these metals contained *d*-orbitals which readily accepted electrons; the higher S.P. value for Cu–Xe compared with that for Zn–Xe was taken as evidence that the *d*-orbitals at a Cu surface were not completely filled. However, the present analysis shows that the transition metal S.P. values are, in general, no higher than expected on the basis of polarisability and field strength. The results also confirm the conclusion of Culver *et al.*,[7] that adsorption of CO on silver and copper is physical.

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