Correlation of Surface Potentials in Physical Adsorption

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Summary Hall's equation describes the qualitative trend in surface potentials of physically adsorbed rare gases correctly but the numerical coefficient is 1·6 rather than 2·25.

HALL[1] showed that surface potentials (S.P.'s) in physical adsorption are proportional to the metal–metal bond strength of the solid (as expressed by the heat of sublimation, ΔH_S) and the polarizability (α) of the adsorbate. Using Mignolet's data[2] he derived the semi-empirical equation (1).

$$\text{S.P.} = 2{\cdot}25 \times \Delta H_S \times 10^{21} \times \alpha \quad (\text{v}) \qquad (1)$$

We have recently measured the S.P.'s of Kr and Xe on films of Ni, Ti, and Mo and found[3] that the general trend is as predicted by Hall but the actual values of the S.P.'s were appreciably lower than those calculated from equation (1). This is illustrated in the Figure for S.P.'s of Xe on different metals. We have included all data available where the thermal history of the surface was stated.

Inspection of the data indicates that the S.P. clearly depends on the history of the films, being lower for sintered films likely to expose a higher proportion of close packed low index planes. We consider that the first factor in Hall's equation involves the adsorption energy, which is lower on close-packed surfaces.[8,10] Although the S.P.'s

Experimental point	Author and reference	Deposition temp. (°K)	Annealing temp. (°K)	Method
1	Mignolet[2]	77	77	capacitor
2	Müller and Roberts[3]	296	296	capacitor
3	Suhrmann *et al.*[4]	90	90	photoelectric
4		90	373	
5	Pritchard *et al.*[5]	298	298	diode and capacitor
6		90;298	298;333	
7		90;333	333	
8	Klemperer and Snaith[6]	77	323	diode
9		293	293	
10		77	293	
11		293	373	
12	Bouwman[7]	77	293	photoelectric
13		77	473	
14		77	573	
15		293	473	
16		77	77	
17		77	473	
18	Rootsaert *et al.*[8]		>2800	FEM[a]
19	Gomer[9]		—	FEM
20	Ehrlich and Hudda[10]		>2300	FEM
21	Nikliborc and Dworecki[11]		—	FEM

[a] Field Emission Microscopy.

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were obtained by different experimental techniques,‡ it is possible to correlate them for similarly treated sintered surfaces according to equation (2). Equation (2) also

$$\text{S.P.} = 1{\cdot}6 \times \Delta H_S \times 10^{21} \times \alpha \quad (\text{v}) \qquad (2)$$

describes well the S.P. data for Kr which confirm Hall's idea on the proportionality of S.P. to α, but these are not plotted because except for our own data[3] (0·4, 0·5, and 0·7 v for Ni, Ti, and Mo, respectively) there was only one value, obtained by FEM at 20°K, reported.[10]

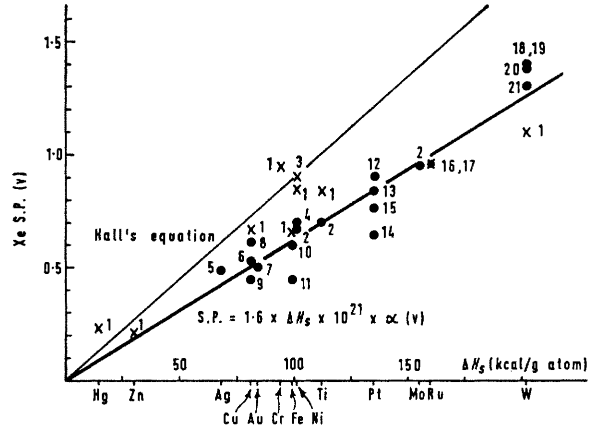

FIGURE. *S.P.'s of* Xe *physically adsorbed on polycrystalline surfaces in correlation with* ΔH_s *of the metals* (ΔH_s *taken from G.C. Bond, "Catalysis by Metals," Academic Press, London and New York,* 1962, *p.* 489); ×, *unsintered surfaces*; ●, *sintered surfaces; experimental points* 1—17 *were obtained for evaporated films,* 18—21 *obtained for the total emitting area of the tips.*

Regarding the discrepancy between equation (1) and the results, even for unsintered films (mainly for metals with higher ΔH_S), it is felt that Hall's method of averaging the data for simple molecules (rare gases) as well as complicated ones (N_2, CO, CH_4, C_2H_2, C_2H_4, and C_2H_6) is responsible. It is difficult to obtain an unambiguous interpretation and hence correlation of the S.P.'s if one includes molecules which possess permanent dipoles and dipoles of higher symmetry.

I have also tried to correlate the S.P.'s of rare gases according to other parameters of the metals, *e.g.* according to the work function as suggested by Suhrmann[12] but this was unsatisfactory.

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‡ The methods based on electron emission are weighted in favour of low work function parts of the total surface.

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