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Effect of surface heterogeneity on physical adsorption

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With 2 tables

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The theoretical procedure developed by Ross and Oliver (1) to describe the monolayer physical adsorption has been tested with two extensions: 1. on the nature of the function used for describing the distribution of adsorptive potential and 2. with the consideration of the variation of the vibrational energy of an adsorbed molecule on different patches by Hoory and Pransnitz (2). They demonstrated that the use of log-normal distribution function instead of the usual gaussian distribution has not improved the results though the former includes only positive adsorption potential values. Secondly, their results indicated that there seems to be no significant advantage in taking into account the variations of vibrational energy from patch to patch.

The present work is an attempt to test these conclusions based upon data reduction for the adsorption of inert gases on Graphitised Carbon. The experimental data on these systems has been taken from reference 1 reported by Comrabis et al. (3). In the present calculations, the values reported by Ross and Oliver for U_{median} and v_{median} were utilised in conjunction with the calculated A_0 , corresponding to this median value. This later assumption means that the variation of vibrational energy between different patches has not been taken into account. Computations have been made for the various assumed values of the heterogeneity parameter " τ " of the log-normal distribution function. The choice of the suitable heterogeneity parameter has been made by the consideration of the least variation of the monolayer saturation volume, with temperature. This procedure has revealed that the same τ value holds good for the adsorption of four different inert gases on the same adsorbent. This observation might be interpreted that the surface exhibits the same kind of distribution of heterogeneous sites for adsorption with no specificity for the physical adsorption of inert gases. These observations offer an interesting case of a heterogeneity parameter in physical adsorption. The values of monolayer saturation volumes for the different gases used together with the parameters employed are summarised in table 1.

The validity of these calculations is also tested with the calculation of the isosteric heat of adsorption. From the values presented in table 2, it could be seen that there is good agreement with reported thermodynamic isosteric heat values, supporting the validity of the assumptions and theoretical methods, employed. The use of a constant value for the parameter A_0 has not significantly affected the results. This could be taken to indicate that the varia-

tions of A_0 over the patches of the surface might not affect the adsorption isotherm of monoatomic gases. The analysis here has been done on all the four gases and is more extensive than those of Hoory and Prausnitz who restricted their analysis to only argon as the adsorbate. The adsorbent chosen in this instant has a narrow distribution while the

Table 1. Monolayer saturation volumes for the four gases on graphitized carbon

Parameter	Neon	Argon	Krypton	Xenon
U_{median} kcal/mole	0.681	2.066	2.754	3.654
$v \times 10^{-12}$ sec $^{-1}$	1.19	1.28	1.00	0.850
τ	0.03	0.03	0.03	0.03
Monolayer saturation Volume ml NTP	5.77	3.66 3.68*) (Ross method) 3.60*) (Point B method)	3.075	2.632

*) At 77.5 °K from ref. 1.

Table 2. Comparison of calculated and thermodynamic isosteric heat of adsorption

Gas	Temp. °K	Isosteric heat of adsorption, calculated in kcal/mole	Thermodynamic value in kcal/mole from ref. 1
Neon	65.9	0.782	0.820
	78.6	0.737	
	94.3	0.827	
Argon	140.6	2.280	2.310
	150.1	2.289	
	166.1	2.304	
	220.4	2.356	
Krypton	245.2	3.05	3.075
	307.2	3.12	
Xenon	279.2	4.056	3.974
	295.9	4.001	
	315.0	4.032	

suitability of log-normal distribution function for wider distribution adsorbents has been tested by Hoory and Prausnitz.

Literatur

- 1) Ross, S. and J. P. Oliver, On Physical Adsorption. (New York, 1964).
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