

## Intermolecular Energy Correlation between Heats of Physical Adsorption of Nonpolar Gases

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A RECENT investigation<sup>1</sup> of the adsorption of nitric oxide and krypton on alkali chloride films has shown that, at low coverage,  $\theta$ , on a particular film, where  $\Phi$  is the equilibrium separation energy<sup>2</sup> for interaction between pairs of like atoms or molecules according to the 9-6 potential function, Aa<sup>-9</sup>-Ba<sup>-6</sup>. The validity of the type of relationship shown by equation (1) has subsequently been

$$\Delta H_{\text{NO}}/\Delta H_{\text{Kr}} \sim \Phi_{\text{NO}}/\Phi_{\text{Kr}} \quad (1)$$

examined for a variety of physical adsorption systems for which heats are given in the literature. The results are conveniently expressed in terms of the correlation function,  $f = \Phi_1\Delta H_2/\Phi_2\Delta H_1$ , where the suffices 1 and 2 refer respectively to argon (or krypton) and any other ad-atom, and the heats correspond to the same value of  $\theta$  on a particular adsorbent. Values of  $f$  for various nonpolar gases adsorbed at low  $\theta$  on alkali halides<sup>1,3-6</sup>, metals,<sup>7-9</sup> charcoal,<sup>10-14</sup> and graphite<sup>15-18</sup> are shown in the Table (only those values which are within 10% of unity are given). In the majority of cases, the

heat for one gas is already known. The method, however, is apparently restricted to nonpolar gases having  $\Phi$  values within the approximate range  $0.42 \times 10^{-14}$  erg (Ne) to  $2.82 \times 10^{-14}$  erg (Xe). Outside this range, the  $f$  values may differ considerably from unity; typical values are: He-Pt black,<sup>7</sup> 9.8; H<sub>2</sub>-charcoal,<sup>12</sup> 6.5; CCl<sub>4</sub>-graphite,<sup>16</sup> 0.65. With N<sub>2</sub>, which has an appreciable quadrupole moment,  $f$  values higher than unity, e.g., NaCl (1.5)<sup>3</sup> and rutile (2.15),<sup>19</sup> reflect the extent of the quadrupole interaction term with ionic crystals. The results for NO (see Table) confirm the previous conclusion<sup>20</sup> that the quadrupole moment of NO is not significant compared with that of nitrogen, although an  $f$  value<sup>1</sup> for NO-LiCl of 1.2 suggests that the quadrupole term may be more appreciable in this case because of the small size of Li<sup>+</sup>.

With the systems shown in the Table, it is evident that factors other than dispersion and repulsion energy are insignificant. This has an important bearing on previous conclusions drawn for certain of these systems. For example, marked

TABLE. Correlation function  $f$  for nonpolar gases

| Neon              | Oxygen             | Methane                         | Krypton            | Nitric oxide               | Xenon                           |
|-------------------|--------------------|---------------------------------|--------------------|----------------------------|---------------------------------|
| Pt (7) 1.04       | NaCl (3) 1.04      | Charcoal (12) 0.93              | KCl (4) 0.93       | NaCl (1) 0.95 <sup>a</sup> | Cu (8) 0.95                     |
| Charcoal (10) 1.0 | CsI (5) 1.03       | Charcoal (14) 1.07 <sup>c</sup> | Pt (7) 0.98        | KCl (1) 0.93 <sup>b</sup>  | Hg (9) 0.89 <sup>a</sup>        |
|                   | CsI (6) 1.10       | Graphon (16) 0.99 <sup>a</sup>  | Charcoal (10) 1.0  | CsCl (1) 1.0 <sup>a</sup>  | Charcoal (11) 1.10 <sup>a</sup> |
|                   | Charcoal (13) 1.04 | Graphon (17) 0.98 <sup>d</sup>  | Graphon (15) 0.94  |                            | Graphon (15) 0.89               |
|                   |                    |                                 | Graphite (18) 1.06 |                            |                                 |

References are shown in parentheses.  $\Delta H_1$  corresponds to Ar value in the same reference, except for: <sup>a</sup>Kr; <sup>b</sup>Ar value in ref. 4; <sup>c</sup>Ar value in ref. 10; <sup>d</sup>Ar value in ref. 15.

heat for argon has been used for  $\Delta H_1$ , but where argon data are not available, the heat for krypton has been used. Except where otherwise stated,  $\Delta H_1$  refers to Ar adsorption under the same conditions (*i.e.*, same reference) as for the ad-atom (specified at the head of each column) corresponding to  $\Delta H_2$ .

The mean of the  $f$  values shown is 0.99 and the standard deviation is 0.06. Thus, the equation,

$$\Delta H \sim c\Phi \quad (2)$$

where  $c$  is a constant for the adsorbent and is independent of the ad-atom, is accurate to within about 4%, and provides a simple method for estimating the heats of physical adsorption of a number of gases on a single adsorbent, when the

discrepancies between calculated and experimental heats of adsorption of inert gases on graphite have been discussed<sup>8</sup> in terms of charge-transfer no-bond interaction, and also polarisation energy, but in view of the present results it is probable that such discrepancies are almost wholly due to lack of knowledge of the real distance of the ad-atom from the surface. The insignificance of the polarisation energy term is also borne out by the value of  $ca$ .  $10^7$  volt cm.<sup>-1</sup> for the field,  $F$ , at a metal surface, calculated in the preceding Communication. For instance, with Xe which has a high polarisability,  $\alpha$ , the term,  $-\frac{1}{2}\alpha F^2$ , is only 0.03 kcal. mole<sup>-1</sup>. Therefore, although polarisation of the ad-atom can give rise to an appreciable surface potential, the contribution to the heat is negligible. These

considerations also show that de Boer and Kruyer's conclusion<sup>21</sup> that the electrostatic term for charcoal generally exceeds the van der Waals term is based on values of  $F$  which are probably too high by a factor of about 10.

The small contribution of the electrostatic term for alkali halides, indicated by the  $f$  values (see Table), has been established previously by the detailed calculations of Orr<sup>6</sup> and Hayakawa.<sup>22</sup>

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