

## CORRIGENDUM. THE ADSORPTION OF DIPOLES

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Communicated by J. K. ROBERTS

Received 1 March 1940

The following correction has to be made to my recent paper on the adsorption of dipoles\*. Equation (10) and the sentence immediately preceding it are to be replaced by the following paragraph:

In the polynomial expressions for  $f_1(x)$  and  $f_2(x)$  the coefficients of the powers of  $x$  depend on  $\eta_2$  and  $\eta_3$  which are functions of  $T$ . When we carry out the differentiation with respect to  $T$  these polynomials are best written as

$$f_1(\epsilon_1 \eta_1, \eta_2, \eta_3), \quad f_2(\epsilon_1 \eta_1, \eta_2, \eta_3), \quad f_1(\epsilon_1, \eta_2, \eta_3), \quad f_2(\epsilon_1, \eta_2, \eta_3)$$

to remind us that  $\epsilon_1, \eta_1, \eta_2$  and  $\eta_3$  are all functions of  $T$ . Differentiating both members of equation (6) with respect to  $T$  we obtain, after rearrangement of the terms,

$$\begin{aligned} & \frac{\partial \epsilon_1}{\partial T} \left[ \theta \{f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) - f_2(\epsilon_1 \eta_1, \eta_2, \eta_3)\} \frac{\partial f_1(\epsilon_1, \eta_2, \eta_3)}{\partial \epsilon_1} \right. \\ & \quad + \theta \eta_1 f_1(\epsilon_1, \eta_2, \eta_3) \frac{\partial}{\partial (\epsilon_1 \eta_1)} \{f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) - f_2(\epsilon_1 \eta_1, \eta_2, \eta_3)\} \\ & \quad \left. - (1 - \theta) f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) \frac{\partial f_2(\epsilon_1, \eta_2, \eta_3)}{\partial \epsilon_1} - (1 - \theta) \eta_1 f_2(\epsilon_1, \eta_2, \eta_3) \frac{\partial f_1(\epsilon_1 \eta_1, \eta_2, \eta_3)}{\partial (\epsilon_1 \eta_1)} \right] \\ = & \frac{V_1 - V}{kT^2} \epsilon_1 \eta_1 \left[ (1 - \theta) f_2(\epsilon_1, \eta_2, \eta_3) \frac{\partial f_1(\epsilon_1 \eta_1, \eta_2, \eta_3)}{\partial (\epsilon_1 \eta_1)} \right. \\ & \quad \left. - \theta f_1(\epsilon_1, \eta_2, \eta_3) \frac{\partial}{\partial (\epsilon_1 \eta_1)} \{f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) - f_2(\epsilon_1 \eta_1, \eta_2, \eta_3)\} \right] \\ & + \frac{V_2}{kT^2} \eta_3 \left[ (1 - \theta) f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) \frac{\partial f_2(\epsilon_1, \eta_2, \eta_3)}{\partial \eta_2} + (1 - \theta) f_2(\epsilon_1, \eta_2, \eta_3) \frac{\partial f_1(\epsilon_1 \eta_1, \eta_2, \eta_3)}{\partial \eta_2} \right. \\ & \quad \left. - \theta \{f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) - f_2(\epsilon_1 \eta_1, \eta_2, \eta_3)\} \frac{\partial f_1(\epsilon_1, \eta_2, \eta_3)}{\partial \eta_2} \right. \\ & \quad \left. - \theta f_1(\epsilon_1, \eta_2, \eta_3) \frac{\partial}{\partial \eta_2} \{f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) - f_2(\epsilon_1 \eta_1, \eta_2, \eta_3)\} \right] \\ & + \frac{V_3}{kT^2} \eta_3 \left[ (1 - \theta) f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) \frac{\partial f_2(\epsilon_1, \eta_2, \eta_3)}{\partial \eta_3} + (1 - \theta) f_2(\epsilon_1, \eta_2, \eta_3) \frac{\partial f_1(\epsilon_1 \eta_1, \eta_2, \eta_3)}{\partial \eta_3} \right. \\ & \quad \left. - \theta \{f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) - f_2(\epsilon_1 \eta_1, \eta_2, \eta_3)\} \frac{\partial f_1(\epsilon_1, \eta_2, \eta_3)}{\partial \eta_3} \right. \\ & \quad \left. - \theta f_1(\epsilon_1, \eta_2, \eta_3) \frac{\partial}{\partial \eta_3} \{f_1(\epsilon_1 \eta_1, \eta_2, \eta_3) - f_2(\epsilon_1 \eta_1, \eta_2, \eta_3)\} \right], \end{aligned}$$

\* Miller, A. R., *Proc. Cambridge Phil. Soc.* 36 (1940), 69.

in which the last two expressions in square brackets on the right-hand side arise from the differentiation of  $\eta_2$  and  $\eta_3$  respectively with respect to  $T$ .

A numerical calculation shows that the contribution of these two extra terms to the variation of the heat of adsorption, which arises only through the third term of the right-hand member of equations (8) or (9), is small. It is zero at the two end-points, and at intermediate points diminishes the value of  $Q - Q_0$ , by an amount of 20 cal. at  $\theta = 0.385$  and of 140 cal. at  $\theta = 0.742$  (see Figs. 2, 3). Thus, this correction has no effect on the conclusions that were drawn in the original paper, namely, that (a) the van der Waals and electrostatic forces make contributions to the heat of adsorption which are opposite in sign and of the same order of magnitude, so that the resultant variation of the heat of adsorption is very much less than would be expected from a consideration of forces of one type only, and (b) the statistical distribution of the particles on the surface has a considerable effect on the variation of the heat of adsorption.

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