

Chemisorption of Gases

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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$4.00 per page) will not be made and no reprints will be furnished free.

Chemisorption of Gases*

SOL WELLER**

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Pittsburgh, Pennsylvania
April 10, 1947

THE question occasionally arises of the appropriateness of including the amount of chemisorbed gas (i.e., that for which the heat of adsorption is comparable with the heats of chemical reactions) when applying the Brunauer-Emmett-Teller (B.E.T.) theory¹ of gas adsorption to an adsorption isotherm. If the first layer of adsorbed gas is chemisorbed, two cases may be distinguished: either the first layer is reversibly adsorbed and partakes in the B.E.T. equilibria, or under the experimental conditions (temperature and time) it is practically irreversibly adsorbed. The latter situation will be favored with short equilibration time and at temperatures so low that the energy required for desorption is much greater than the thermal energy (RT).

If the first layer is irreversibly adsorbed, it does not take part in the equilibrium relations of the B.E.T. theory, and for the purposes of the theory it may be considered to form part of the solid surface. The theory will then apply to the balance of the adsorbed gas, i.e., to the total adsorption minus the chemisorption. If the solid surface is uniform and is completely covered by the chemisorbed gas, the total adsorption, expressed as the statistical number of layers of gas adsorbed, will in this case be given by

$$n = \frac{v}{v_m} = 1 + \frac{cx}{(1-x)[1+(c-1)x]}, \quad (1)$$

where $c = p_0(a_1/b_1)e^{(E_1-E_L)/RT}$, E_2 =heat of adsorption for the second layer, $E_3=E_4=\dots=E_L$.

On the other hand, the case in which the chemisorbed gas does participate in the statistical equilibria is included in the B.E.T. theory without any special treatment. In this situation, if E_1 , the heat of adsorption of the first (chemisorbed) layer, is unique and $E_2=E_3=\dots=E_L$, the simple B.E.T. theory applies and the total adsorption is given by

$$n = \frac{v}{v_m} = \frac{cx}{(1-x)[1+(c-1)x]}, \quad (2)$$

where $c = p_0(a_1/b_1)e^{(E_1-E_L)/RT}$. However, the high value of E_1 implies strong binding between the chemisorbed layer

and the solid surface, and it is exactly in this situation that one expects E_2 as well as E_1 to be unique and different from E_L . The reasonable assumption that $E_1 \neq E_2 \neq E_3 = E_4 = \dots = E_L$ leads to an interesting result. This case was worked out by Brunauer, Emmett, and Teller.¹ It can be shown that the number of adsorbed layers is expressible in the form

$$n = \frac{v}{v_m} = \frac{cx[(1-x)^2 + kx(2-x)]}{(1-x)[(1-x)(1+cx) + ckx^2]}, \quad (3)$$

where $c = p_0(a_1/b_1)e^{(E_1-E_L)/RT}$ and $k = p_0(a_2/b_2)e^{(E_2-E_L)/RT}$. Now if E_1 is very large, as it is for chemisorption, c is also large and $cx \gg 1$ for all values of x usually studied (e.g., $x > .05$). In this case, the term 1 may be neglected in comparison with cx in the denominator of Eq. (3), and Eq. (3) becomes

$$n = \frac{v}{v_m} = \frac{(1-x)^2 + kx(2-x)}{(1-x)(1-x+kx)} = \frac{1-2x+x^2+kx-kx^2+kx}{1-2x+x^2+kx-kx^2},$$

or

$$n = \frac{v}{v_m} = 1 + \frac{kx}{(1-x)[1+(k-1)x]}, \quad (4)$$

It will be seen that Eq. (4) is identical with Eq. (1), and k has exactly the same significance in Eq. (4) as does c in Eq. (1). This means that when both physical adsorption and chemisorption occur, and if the approximation that E_1 and E_2 are unique and $E_3=E_4=\dots=E_L$ is good, then the total adsorption is given by Eq. (2) or Eq. (4) regardless of whether or not the chemisorption is reversible.

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¹ Brunauer, Emmett, and Teller, J. Am. Chem. Soc. **60**, 309 (1938).

² Equations (1) and (4) involve the implicit assumption that the packing of adsorbed molecules is the same in the first layer as in subsequent layers. If this is not true, the term unity on the right of the equation will be replaced by v_m'/v_m , where v_m' and v_m are, respectively, the volumes of "chemisorbed" and "physically adsorbed" gas required to form a monolayer.

Errata: On the Dissociation Energies of CO, N₂, NO, and CN

[J. Chem. Phys. **14**, 568 (1946)]

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STYLISTIC changes made by the kindness and courtesy of the editors have accidentally altered the meaning of the original text.

The second sentence of the paper should read: "Their paper shows that even the correlation of those authors leads to contradictions with such a non-crossing rule for the excited states who consider . . ." instead of: "Their paper shows that even their correlation leads to contradictions with such a non-crossing rule for the excited states since they consider. . ."

In the 13th line of the text "Moreover" should be replaced by "On the other hand"; in the 15th line "other" by "some."