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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 (\$3.00 per page) will not be made and no reprints will be furnished free.

Theory of Multimolecular Adsorption from a Mixture of Gases

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October 29, 1945

THE purpose of the present note is to outline a possible way of extending the Brunauer-Emmett-Teller¹ (BET) theory of multimolecular adsorption to the case of a mixture of two gases. The problem will be discussed in more detail in a later paper, including applications and the treatment for any number of gases.

We consider the adsorption of two gases A and B at relative pressures $x_A = p_A/p_A^0$ and $x_B = p_B/p_B^0$, and at a temperature T below both critical temperatures. Let q_A , q_B , q_{AA} , q_{BB} , q_{AB} , q_{BA} , q_{ANA} , and q_{BNA} , be, respectively, the heats of adsorption per mole of A on the bare surface, B on the bare surface, A on a layer of pure A, B on a layer of pure B, A on a layer of pure B, B on a layer of pure A, A on a layer of composition N_A (mole fraction of A), and B on a layer of composition N_A . Let s_i represent the surface area covered by i layers of adsorbed molecules. Then, at equilibrium,

$$\begin{cases} a_{AS}p_A = b_{AS}N_{A1} \exp(-q_A/RT), \\ a_{BS}p_B = b_{BS}(1-N_{A1}) \exp(-q_B/RT), \\ a_{Ai-1}p_A = b_{Ai}N_{Ai} \exp(-q_{ANA(i-1)}/RT), \\ a_{Bi-1}p_B = b_{Bi}(1-N_{Ai}) \exp(-q_{BNA(i-1)}/RT). \end{cases} \quad (1)$$

The above equations use average heats of adsorption and they assume that the energy of attachment of a molecule on top of the $(i-1)$ th layer (to become a member of the i th layer) depends on the composition of the $(i-1)$ th layer only. If we consider similar equilibria for the evaporation and condensation of A from pure A and B from pure B, we have

$$\frac{v_A}{v_m^A} = \frac{(s_1 + s_2 + \dots + s_n)N_{A1} + (s_2 + \dots + s_n)N_{A2} + \dots + s_n N_{An}}{s_0 + s_1 + \dots + s_n} \quad (10)$$

$$= \frac{E_0[(1 + E_1 + E_1E_2 + \dots + E_1E_2 \dots E_{n-1})N_{A1} + (E_1 + \dots + E_1E_2 \dots E_{n-1})N_{A2} + \dots + E_1 \dots E_{n-1}N_{An}]}{1 + E_0(1 + E_1 + E_1E_2 + \dots + E_1E_2 \dots E_{n-1})} \quad (11)$$

From Eqs. (7) and (8):

$$\lim_{i \rightarrow \infty} N_{Ai} = N_A = x_A Q_{AB}^\beta / E, \quad (12)$$

$$\lim_{i \rightarrow \infty} E_i = E = x_A Q_{AB}^\beta + x_B Q_{BA}^\alpha. \quad (13)$$

$$\begin{aligned} a_{AS}p_A^0 &= b_{AS} \exp(-q_{AA}/RT), \\ a_{BS}p_B^0 &= b_{BS} \exp(-q_{BB}/RT) \end{aligned}$$

or

$$\begin{aligned} \frac{b_A}{a_A} &= p_A^0 \exp(q_{AA}/RT), \\ \frac{b_B}{a_B} &= p_B^0 \exp(q_{BB}/RT). \end{aligned} \quad (2)$$

We make the approximation, as is done in the BET theory, that second and higher layers have the same evaporation-condensation properties as the liquid state. Thus, in the present case, it seems appropriate to assume that q_{ANA} and q_{BNA} can be obtained from the vapor pressure curves for a binary liquid mixture of A and B at the same temperature. As a good approximation,² we can write for the equations of these vapor pressure curves

$$\begin{aligned} x_A &= N_A \exp[(q_{AA} - q_{AB})(1 - N_A)/RT], \\ x_B &= (1 - N_A) \exp[(q_{BB} - q_{BA})N_A/RT]. \end{aligned} \quad (3)$$

One can of course use other equations in place of Eqs. (3), or, in fact, use the experimental vapor pressure curves if available. We can get corresponding equations involving q_{ANA} and q_{BNA} by considering equilibria of the type used to obtain Eq. (2):

$$\begin{aligned} a_{AS}p_A &= b_{AS}N_A \exp(-q_{ANA}/RT), \\ a_{BS}p_B &= b_{BS}(1 - N_A) \exp(-q_{BNA}/RT); \end{aligned}$$

or, from Eq. (2),

$$\begin{aligned} x_A &= N_A \exp[(q_{AA} - q_{ANA})/RT], \\ x_B &= (1 - N_A) \exp[(q_{BB} - q_{BNA})/RT]. \end{aligned} \quad (4)$$

Comparing Eqs. (3) and (4), we see that

$$\begin{aligned} q_{AA} - q_{ANA} &= (q_{AA} - q_{AB})(1 - N_A)^2, \\ q_{BB} - q_{BNA} &= (q_{BB} - q_{BA})N_A^2. \end{aligned} \quad (5)$$

If Eqs. (2) and (5) are now substituted into Eqs. (1), one finds

$$s_i = s_{i-1}E_{i-1} = s_0E_0E_1E_2 \dots E_{i-1}, \quad i = 1, 2, \dots \quad (6)$$

$$\begin{cases} E_0 = x_A Q_A + x_B Q_B, \\ E_i = x_A Q_{AB}^{\beta(i)} + x_B Q_{BA}^{\alpha(i)}, \\ \alpha(i) = N_{Ai}^2, \quad \beta(i) = (1 - N_{Ai})^2, \end{cases} \quad i = 1, 2, \dots \quad (7)$$

$$\begin{cases} N_{A1} = x_A Q_A / E_0, \\ N_{Ai} = x_A Q_{AB}^{\beta(i-1)} / E_{i-1}, \end{cases} \quad i = 2, 3, \dots \quad (8)$$

$$\begin{cases} Q_A = \exp[(q_A - q_{AA})/RT], \\ Q_B = \exp[(q_B - q_{BB})/RT], \\ Q_{AB} = \exp[(q_{AB} - q_{AA})/RT], \\ Q_{BA} = \exp[(q_{BA} - q_{BB})/RT]. \end{cases} \quad (9)$$

If v_A and v_m^A are the volume of A adsorbed and the volume of A necessary to give a complete unimolecular layer, respectively, then³

It will be noted that v_A/v_m^A and v_B/v_m^B become infinite (condensation) when $E=1$ and $n=\infty$. Putting $E=1$ in Eqs. (12) and (13) gives Eqs. (3), as expected.

It appears that Eq. (11) may be approximated to within several percent in most cases of interest by

$$\frac{v_A}{v_m^A} \approx \frac{E_0 \{ N_{A1}(E^{n+1} - E^n - E + 1) + N_A[(n-1)E^{n+1} - nE^n + E] \}}{(1-E)[1-E-E_0(E^n-1)]} \quad (14)$$

and, for $n = \infty$, by

$$\frac{v_A}{v_m^A} \approx \frac{E_0[N_{A1}(1-E) + N_A E]}{(1-E)(1-E+E_0)} \quad (15)$$

The quantity v_B/v_m^B may be obtained from Eqs. (10), (11), (14), and (15) by replacing N_A by $1-N_A$.

If $x_B=0$, these equations reduce to the usual BET equations with $N_A=1$, $E=x_A=x$ and $E_0=x_A Q_A=xc$.

In comparing theory with experiment, Q_A , Q_B , v_m^A , and v_m^B may be found from the pure A and pure B isotherms, while the vapor pressure curves can be used to give Q_{AB} and Q_{BA} .

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

²See, for example, R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), p. 357.

³It is an approximation to use mole fractions instead of area fractions in Eqs. (10), (11), (14), and (15) unless the molar volumes of A and B are equal. This will be discussed in a later paper.

A General Theory of the Reaction Loci in Emulsion Polymerization. II*

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October 18, 1945]

THE earlier theory¹ has been extended to explain how two minor loci can act, either after soap micelles disappear in polymerization with soap or when no initial soap is used:

A. Loci for the initiation of polymer particle nuclei.

1. Soap micelles: When an initial soap concentration of about 3 percent is used (with 100 g monomer to 180 g water), nearly all of the polymer particle nuclei are initiated in the micelles. With more soap the polymer particles at any given yield are more numerous and smaller, and with less soap less numerous and larger. For example, an isoprene-styrene polymer at 40-percent yield gave diameters of 375A and 485A in 4-percent and 1-percent potassium myristate solutions.
2. Water: The aqueous phase, *excluding* soap micelles and polymer-monomer particles, is a secondary locus whose *relative* prominence increases as soap disappears from its micelles due to adsorption of soap molecules around the monomer-polymer (latex) particles. Finally (e.g., at a 60-percent yield) by process 4, below, too few molecules of monomer remain to make this locus effective.
3. Monomer droplets: The new evidence indicates that monomer droplets are relatively unimportant in initiating new polymer particles, since thus far no evidence has been obtained to show that a monomer droplet can do more than change into a polymer particle of much smaller size.

B. Loci for the formation of polymer.

4. Polymer-monomer particle: Almost all of the polymer is produced in this locus. (See Communication I.)
5. Monomer-emulsion droplets: The principal function of the monomer droplet is to act as a reservoir from which monomer diffuses through a seemingly thick diffusion layer into the other loci. In static experiments every emulsion monomer droplet observed changed into a very much smaller polymer droplet when suspended in a soap solution at 40° to 50°C with all of the necessary reagents present.

Water: Evidence that water (with 0.2 percent of potassium persulfate as catalyst) can act as a locus for the initiation of polymer particle nuclei is given by experiments (1) by Stearns and (2) by Corrin. (1) A flask partly filled with this aqueous phase has two side tubes, turned downward, sealed into the neck. In the bottom of one of these is isoprene, or styrene, or other monomers, and in the bottom of the other a mercaptan. The system is evacuated through the neck of the flask, which is then sealed off, after which the whole system is suspended inside the water of a thermostat held at 50°C for 18 hours. In two experiments of this type with styrene, the diameters of the polymer particles obtained by Oppenheimer were 1500 and 2000A, respectively, while the numbers were 37×10^{11} and 5.6×10^{11} per cu. cm: with isoprene the values were 2200A and 2.9×10^{11} . (2) The polymerization of styrene in water and salt solutions was investigated in the absence of the water-monomer interface. Tubes with sealed-in inner cups were employed to insure a short vapor path between the bulk styrene and water. The tubes were maintained in a 40°C bath for 42 hours. The solutions contained 0.1 percent potassium persulfate, and any salt added was potassium chloride. (Table I.)

Since at 50°C a molecule of mercaptan in the water is readily converted by the catalyst into a free radical (in (2) no mercaptan is present, so styrene itself forms the initial free radical), which can unite with a monomer molecule to give a larger free radical and again with more monomer molecules, until the growing chain is terminated, the results cited above accord with expectations. They indicate that the aqueous phase, after the disappearance of soap, can act as a locus for initiation of polymer particles.

Locus of polymerization in monomer droplets (Stearns). A drop of styrene or isoprene with 0.2 percent lauryl mercaptan was suspended in an aqueous solution of 3 percent potassium laurate, 0.3 percent potassium ferricyanide, 0.1 percent potassium persulfate, and 1 percent sodium car-

TABLE I.

% K ₂ S ₂ O ₈	m KCl	$\mu \times 10^2$ (μ = ionic strength)	Conversion (mg/cc)	Mean particle diameter in A	Number of particles per cc
0.1	0.0	1.11	2.89	1710	1.1×10^{11}
0.1	0.0025	1.36	2.99	1310	2.5×10^{11}
0.1	0.005	1.61	3.08	1370	2.3×10^{11}
0.1	0.01	2.11	2.82	2870	2.3×10^{11}
0.1	0.05	6.11	2.47	*	*
0.1	0.10	11.1	1.74	*	*