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

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$$\frac{v_A}{v_m{}^A} \cong \frac{E_0\{N_{A_1}(E^{n+1}-E^n-E+1) + N_A[(n-1)E^{n+1}-nE^n+E]\}}{(1-E)[1-E-E_0(E^n-1)]} \quad (14)$$

and, for $n = \infty$, by

$$\frac{v_A}{v_m{}^A} \cong \frac{E_0[N_{A_1}(1-E)+N_A E]}{(1-E)(1-E+E_0)}. \quad (15)$$

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}.

[1] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).
[2] See, for example, R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), p. 357.
[3] It 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 theory[1] 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.

% $K_2S_2O_8$	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	*	*

bonate at 40° or 50°C. The principal phenomenon observed was that 0.999 of the volume disappeared by diffusion of the monomer into the soap solution. However, in every one of numerous experiments the monomer droplet gradually changed into a monomer-polymer droplet.

After the drop was reduced to about a tenth its original diameter, diffusion into the soap solution ceased, since the droplet remaining consisted largely of polymer. In some cases the density was higher than that of water (plus soap), shown by its falling downward through the water. In general, the drop became deformed, becoming non-spherical as its content of polymer increased.

* The work reported in this paper was done in connection with the Government Research Program on synthetic rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.
[1] W. D. Harkins, J. Chem. Phys. 13, 381 (1945).

The Density and Thermal Expansion of Liquid Phosgene

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December 10, 1945

1. INTRODUCTION

SOME unpublished values for the density of liquid phosgene suggested that the figures available in chemical literature might be high. The measurements described in the present paper confirmed this view; they were carried out on two samples, from the same source, which had been shown by chemical analysis to contain only traces of impurity too small to affect the density within the accuracy of the determinations.

2. EXPERIMENTAL METHOD

A bulb was blown on thick-walled Pyrex capillary tubing and the volume per cm of stem determined over the working range by using a cathetometer to measure distances of the meniscus of mercury charges of known weight from a mark on the tube. The volume up to this mark was 1.7505

TABLE I.

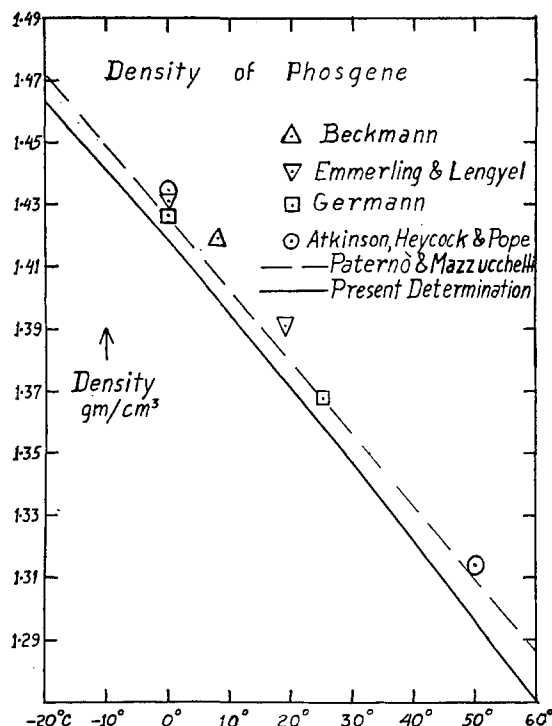| First series		Second series	
Temperature	Density	Temperature	Density
−9.35°C	1.444$_1$ g/cm³	20.05°C	1.373$_0$ g/cm³
−8.60	1.442$_1$	20.10	1.371$_4$
−7.75	1.439$_7$	27.00	1.354$_7$
−5.70	1.434$_8$	37.00	1.331$_0$
−3.25	1.429$_0$	45.45	1.309$_4$
−2.70	1.427$_7$	48.50	1.301$_9$
−2.00	1.426$_0$	19.20	1.374$_5$
−0.65	1.422$_4$	14.50	1.385$_3$
−0.05	1.421$_4$	5.00	1.407$_6$
15.03	1.383$_9$	0.00	1.418$_7$
16.73	1.380$_3$	−5.00	1.428$_8$
20.59	1.370$_9$	−10.00	1.440$_8$
28.01	1.353$_3$	−15.00	1.451$_3$
34.66	1.336$_2$	−20.00	1.463$_1$
40.13	1.322$_9$	20.00	1.371$_4$
45.27	1.309$_3$		
50.75	1.295$_1$		
55.50	1.283$_1$		
60.20	1.270$_6$		
17.75	1.378$_3$		
12.00	1.391$_4$		
7.55	1.402$_2$		
−0.20	1.420$_7$		
−6.10	1.434$_8$		
−10.40	1.445$_0$		
−15.50	1.457$_6$		

FIG. 1.

±0.0004 cm³ and the tube diameter was about 4 mm. Phosgene was distilled in and the tube sealed. The position of the phosgene meniscus was then determined at temperatures from −20°C to +60°C. The mass of phosgene was corrected for the mass in the vapor phase using the vapor pressures of Paternò and Mazzucchelli.[1] Corrections were also applied for the meniscus, and weighings were reduced to vacuum. Two series of experiments, in the order given below, were carried out independently on different samples.

Possible errors caused by the expansion of the bulb under pressure and temperature were shown to be negligible.

3. EXPERIMENTAL RESULTS

The results given in Table I, taking both series together, have been fitted by the method of least squares with the following regression curve:

$$\rho = 1.42014 - 0.0023120t - 0.000002872t^2$$
$$= 1.42014 (1 - 0.001628t - 0.000002022t^2),$$

where ρ is the density in gm/cm³ at t°C.

By differentiating this equation the thermal expansion per degree centigrade was found to have the following values:

Temperature	$1/v(dv/dt)$
50°C	0.002003
30	0.001842
10	0.001696
−10	0.001563

Above 0°C the agreement between the two series and of each with the equation is better than 0.1 percent. Below