

The Density and Thermal Expansion of Liquid Phosgene

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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SOME unpublished values for the density of liquid phosgene suggested that the figures available in chemical literature might be high.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 Temperature	Density	Second series Temperature	Density
-9.35°C	1.444 ₁ g/cm ³	20.05°C	1.373 ₀ g/cm ³
-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 ₀
-2.00	1.426 ₀	19.20	1.374 ₅
-0.65	1.422 ₄	14.50	1.385 ₂
-0.05	1.421 ₄	5.00	1.407 ₆
15.03	1.383 ₃	0.00	1.418 ₇
16.73	1.380 ₃	-5.00	1.428 ₈
20.59	1.370 ₀	-10.00	1.440 ₀
28.01	1.353 ₃	-15.00	1.451 ₀
34.66	1.336 ₂	-20.00	1.463 ₁
40.13	1.322 ₃	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		

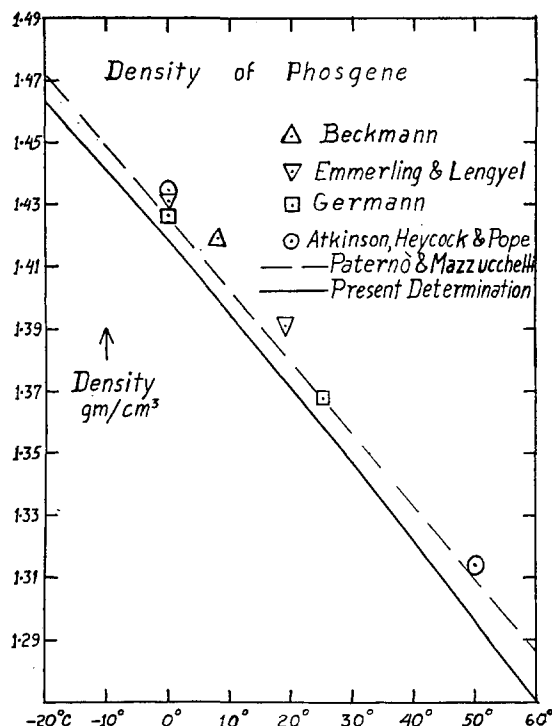


FIG. 1.

± 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 $t^\circ\text{C}$.

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

Temperature	$1/\rho(d\rho/dt)$
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

zero the scatter increases but is always less than 0.2 percent. This may be attributed to more accurate temperature control during the determinations at the higher temperatures.

4. COMPARISON WITH PREVIOUS DETERMINATIONS

Paternò and Mazzucchelli¹ give an equation based on experiments over the range -15.4°C to $+59.9^{\circ}\text{C}$ which is about 0.6 percent above the present data at 20°C and gives a slightly lower coefficient of expansion.

Atkinson, Heycock, and Pope² found still higher densities and exceed the latest figures by about 1.2 percent.

Germann³ only did determinations at 0°C and 25°C and agrees closely with Paternò and Mazzucchelli.

Figures given by Emmerling and Lengyel⁴ and Beckmann⁵ are fairly close to Atkinson, Heycock, and Pope.

All these determinations may be compared with the present findings (see Fig. 1). It is significant that the older values are high which suggests that the presence of carbon tetrachloride might explain the discrepancies. About 6 percent would raise the density of phosgene by 1 percent and the deviation would tend to increase with rise of temperature as is observed in the case of the Italian data. It is probable that dissolved chlorine would also raise the density. The results of Atkinson, Heycock, and Pope were obtained by chemical estimation of the phosgene instead of direct weighing. It is not possible to draw any conclusions from the methods of manufacture of the phosgene since various processes have been used and no correlation with the observed densities is apparent.

5. SUMMARY

A determination of the density and thermal expansion of liquid phosgene over the range -20°C to $+60^{\circ}\text{C}$ is described. The density in this range is given by the following equation:

$$\rho = 1.42014 - 0.0023120t - 0.000002872t^2.$$

6. ACKNOWLEDGMENT

These experiments were carried out in a Ministry of Supply Research Establishment and the results are published by permission of the Director General of Scientific Research and Development.

¹ Paternò and Mazzucchelli, *Gazzetta* [1] **50**, 30 (1920).

² Atkinson, Heycock, and Pope, *J. Chem. Soc. Trans.* **2**, 1410 (1920).

³ Germann, *J. Phys. Chem.* **29**, 138 (1925).

⁴ Emmerling and Lengyel, *Ann. Suppl.* **7**, 106 (1870); *Berichte* **2**, 546 (1869).

⁵ Beckmann, *Zeits. f. Ann. Chem.* **55**, 371 (1907).

Statistical Mechanics of Linear Association Equilibria

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November 21, 1945

IN a recently published paper Tobolsky and Blatz¹ have discussed the "possible application" of the lattice model for mixtures of linear polymers with small molecules to reversible associations of liquids such as the alcohols and their solutions in non-associated solvents.

It appears that they were unaware that this particular problem can be treated by previously derived relationships pertaining to heterogeneous polymer-solvent mixtures.² Their paper contains the unfounded and misleading statement, "... whereas Flory² was considering stable polymer molecules which did not change their size distribution when diluted, we are here concerned with the problem of reversible association. . . ." It is the writer's purpose to emphasize here the generality of the previously derived thermodynamic functions as applied to equilibria involving transformations between various polymeric species.

In applying the methods of thermodynamics, or statistical mechanics, to chemical equilibrium problems the character of the bonds, or intermolecular forces, subject to equilibration need not be specified. The treatment, previously presented, of equilibria involving polymer molecules is completely general, and although secondary valence polymers were not mentioned, it should have been clear that it is also applicable to these as well, provided that the "polymers" consist predominantly of linear sequences of structural units. This treatment led to the conclusion that the equilibrium constant for processes involving polymeric substances assumes the same form as that for the analogous reaction between monomeric species; the relationship of the equilibrium constant to the standard state free energy change is the same in the two cases. Thus, no modifications in the formulation of equilibrium constants are occasioned by the configurational randomness of the polymeric reacting species.

For the purpose of applying this principle to associative equilibria specifically, consider a solution containing N_0 associating units per unit volume, each of which is capable of entering into two "bonds" to form linear polymers. If each of these bonds forms independently of the presence or absence of other bonds attached to the adjoining units, then an equilibrium constant governing the associative process can be written

$$K = p/(1-p)^2 N_0, \quad (1)$$

where p (equivalent to the "y" of Tobolsky and Blatz) is the "degree of association," i.e., $N_0 p$ represents the concentration of association bonds at equilibrium. Also from the above assumptions and the nature of the dependence of partial molal free energies on concentrations, it follows that the molecular size distribution is given by

$$N_x = N_0(1-p)^2 p^{x-1}, \quad (2)^{3,4}$$

where N_x represents the molar concentration of x -mers; the number average degree of polymerization, according to (2), is given by

$$\bar{x}_n = 1/(1-p), \quad (3)$$

the partial molal free energy of the solvent in this system is obtained directly by substituting (3) into Eq. (17) of reference 2, giving

$$\Delta \bar{F}_1 = RT[\ln(1-v_2) + v_2 p + \mu v_2^2], \quad (4)$$

where v_2 is the volume fraction of solute including all species, and μ is a semi-empirical parameter^{5,6} in which is included the heat of dilution term. Equation (4) is identical