

# Thermodynamics of High Polymer Solutions

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darkening of a given spot was taken as a measure of the intensity of the diffracted x-ray beam producing the spot.

The exposure required to produce a density  $\rho$  is given by the product  $Et$ , where  $E$  is the illumination and  $t$  the time. The product  $Et$  is a constant for a given density as long as the development time is constant, but both  $E$  and  $t$  may vary. Letting  $\rho$  equal the density of silver deposit which is just visible,  $Et$  is the exposure necessary to produce darkening which is just observable.

If a film be printed for such a time  $t_1$  that one of the reflections, 200 for instance, just begins to be darkened, and for such a time  $t_2$  that another reflection, 400, just begins to be darkened, then the relative densities of the spots are given by the ratio of  $t_1$  to  $t_2$ . That is, if  $t_1$  is twice  $t_2$ , then 200 is twice as dense as 400. This result follows from the fact that the product  $E_1 t_1$  must be equal to  $E_2 t_2$ . Any variation in  $t$  must be accompanied by an inverse variation in  $E$ . The illumination  $E$  is inversely proportional to the density of the spot, and therefore the density is directly proportional to the time  $t$  required to produce an observable darkening. To a first approximation, the density of the silver deposit is directly proportional to the intensity of the diffracted x-ray beam. Thus, it is apparent that a measure of the intensity of any reflection relative to all others on the same film is given by the time required to bring out a silver deposit just visible to the eye.

There are, of course, limitations to this procedure. The density of a reflection is not uniform over the spot. Some one part must be chosen as a reference point, the center being the easiest. The scale of values obtained does not represent the true intensities since the intensities are not integrated over the entire spots. However, the results are highly satisfactory when only a relative scale is needed.

It should be pointed out that a printing paper which can be developed to a high contrast should be used. The higher the contrast, the greater the resolution of the spots. A paper manufactured by the Eastman Kodak Company under the trade name "Kodolith" was found suitable when developed for ten minutes.

The author is indebted to A. C. Hardy of the Massachusetts Institute of Technology for suggestions which led to the development of this method of estimating intensities.

### The Vapor Pressure and Heat of Vaporization of $N^{15}$ \*

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June 25, 1941

INTEREST in the separation of isotopes and in the theory of vapor pressures of non-polar liquids has led to the investigation of the vapor pressures of various isotopic substances. This is a preliminary report on the vapor pressure difference between natural nitrogen and nitrogen containing 34.6 percent  $N^{15}$ , with the equilibrium amounts of  $N^{14}_2$ ,  $N^{14}N^{15}$ , and  $N^{15}_2$ .

The differential method and the apparatus used in making these measurements are similar to those used by Thode<sup>1</sup> but differ in several essential details which will be

TABLE I.

$P_1$ CM	TEMP. °K	$P_1 - P_2$ CM	$P_1/P_2$
11.250	64.11	0.0480	1.00428
19.900	67.50	0.0771	1.00389
25.100	69.00	0.0921	1.00368
31.110	70.46	0.1081	1.00349
42.022	72.61	0.1368	1.00327
54.500	74.61	0.1646	1.00303

described in a later paper. The nitrogen samples were obtained by circulating ammonia over hot copper oxide. The ammonia was prepared from C.P. ammonium chloride. The various samples of nitrogen were purified by the use of liquid nitrogen traps and were analyzed for purity and isotopic content on a Bleakney type mass spectrometer. Two samples of natural nitrogen were also tested by measuring the differences in vapor pressure between them from 64°K to 75°K. These differences were in no case larger than the experimental error.

Table I briefly summarizes the results. Two different samples of natural nitrogen and of the concentrated nitrogen were used in obtaining these results.  $P_1$  is the pressure of natural nitrogen and  $P_2$  is the pressure of the nitrogen containing 34.6 percent  $N^{15}$ . Each  $P_1 - P_2$  is an average of at least four determinations on the samples, where each determination is the average of at least ten readings taken two minutes apart. The absolute temperature was deduced from the observed vapor pressure of the ordinary nitrogen using the data of Henning and Otto<sup>2</sup> and is correct to  $\pm 0.01^\circ$ . The experimental error in  $P_1 - P_2$  is in all cases less than  $\pm 1.4$  percent of the difference, usually being  $\pm 1$  percent.

The vapor pressure data for the liquids can be represented by an equation of the form,  $\log_{10} (P_1/P_2) = A/T + B$ . Using this,  $\Delta H_2 - \Delta H_1$  was calculated to be 1.13 calories. Assuming that the difference in the heats of vaporization is a linear function of the mole fraction, the heat of vaporization of pure  $N^{15}_2$  was found to be 3.27 calories higher than the heat of vaporization of ordinary nitrogen.

A more detailed report of these results, together with the results of work on more concentrated samples of  $N^{15}$  and extending over a somewhat larger temperature range, will be reported later. The author gratefully acknowledges his indebtedness to Professor H. C. Urey for suggesting these experiments and for his helpful advice throughout the course of the work.

<sup>1</sup> Harry G. Thode, J. Am. Chem. Soc. **62**, 581 (1940).

<sup>2</sup> Henning and Otto, Physik. Zeits. **37**, 634 (1936).

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### Thermodynamics of High Polymer Solutions

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July 14, 1941

THE abnormal thermodynamic properties of solutions containing high polymers have been explained quantitatively by Meyer<sup>1</sup> in terms of an idealized model in which elements of the polymer chains replace molecules

of solvent in a quasi-solid lattice. Entropies of mixing exceeding the classical "ideal" values are attributed to the numerous configurations which the polymer molecules are free to assume. Huggins<sup>2</sup> has reported an approximate treatment of dilute polymer solutions, apparently assuming a model equivalent to that of Meyer. Some time ago the writer carried out, on the basis of Meyer's model, a general statistical treatment applicable to high polymer solutions at all concentrations. The entropy of mixing  $n$  solvent and  $N$  polymer molecules, each of which possesses  $x$  elements which may replace  $\beta$  molecules of solvent in the liquid lattice is found to be

$$\Delta S_{\text{mixing}} = k \left[ -n' \ln \left( \frac{n'}{n' + xN} \right) - N \ln \left( \frac{N}{n' + xN} \right) + (x-1)N \ln \left( \frac{\gamma-1}{e} \right) - N \ln 2 \right], \quad (1)$$

where  $n' = n/\beta$  and  $\gamma$  is the coordination number for a polymer chain element in the liquid lattice. This equation differs markedly from the familiar expression for the entropy of mixing equal sized molecules. However, (1) reduces to the latter when  $x=1$ , provided that the last term, which takes into account the indistinguishability of one end of the polymer molecule from the other, is omitted. Very recently Huggins<sup>3</sup> has derived an analogous relationship for the case  $\beta=1$ .

The partial molal entropy of dilution, obtained from (1), is

$$\Delta \bar{S}_1 = -(R/\beta) [\ln (1-v_2) + (1-1/x)v_2], \quad (2)$$

where  $v_2 = xN/(n' + xN)$  is the volume fraction of polymer in solution. Series expansion gives

$$\Delta \bar{S}_1 = (R/\beta)(v_2/x + v_2^2/2 + v_2^3/3 + \dots). \quad (2')$$

Osmotic pressure data<sup>4</sup> for dilute solution of rubber in toluene ( $\Delta \bar{H}_1 \approx 0$ ) agree with (2') if one lets  $\beta=6$ . Data for

concentrated solutions ( $v_2 > 0.5$ ) require a value of  $\beta$  in the vicinity of unity. Equation (2) predicts, in agreement with experiments,<sup>5</sup> that the partial pressure of solvent in a concentrated solution of a high polymer will be practically independent of molecular weight.

Assuming<sup>6</sup> a heat of dilution given by  $\Delta \bar{H}_1 = B\bar{V}_1 v_2^2$  where  $\bar{V}_1$  is the partial molar volume of the solvent, the critical condition for complete miscibility when  $\beta=1$  is found to be  $B\bar{V}_1/RT = (1+x^2)/2x$ ; the critical concentration, which is given by  $v_2 = 1/(1+x^2)$ , lies close to  $v_2=0$  for high polymers. Detailed calculations of the composition of the phases in equilibrium for  $x=1000$  when  $B\bar{V}_1/RT$  exceeds slightly the critical value (i.e., slightly below the critical solution temperature) show that there will be negligible amounts of polymer in the solvent phase, even when the polymer phase contains as much as 80 percent of solvent. Thus, the statistical mechanical treatment of polymer solutions explains the results of Brønsted and Volqvartz,<sup>7</sup> who found that polystyrene was capable of taking up several times its weight of propyl laurate at 20° without dissolving to a perceptible extent in the excess solvent. A discussion of the bearing of this work on fractional separation of non-homogeneous polymers will be included in a forthcoming publication.

From (1) it can also be shown that, according to Meyer's model, the molar entropy change for the conversion of completely oriented polymer to a state of random entanglement is given by

$$R \ln (x/2) + R(x-1) \ln [(\gamma-1)/e]. \quad (3)$$

<sup>1</sup> Meyer, *Helv. Chim. Acta* **23**, 1063 (1940).

<sup>2</sup> M. L. Huggins, *J. Chem. Phys.* **9**, 440 (1941).

<sup>3</sup> M. L. Huggins, paper presented before the Wilder D. Bancroft Colloid Symposium, Ithaca, New York, June 20, 1941.

<sup>4</sup> Meyer, Wolff, and Boissonnas, *Helv. Chim. Acta* **23**, 430 (1940).

<sup>5</sup> Stamberger, *J. Chem. Soc.* 2318 (1929).

<sup>6</sup> G. Scatchard, *Chem. Rev.* **8**, 321 (1931).

<sup>7</sup> J. N. Brønsted and K. Volqvartz, *Trans. Faraday Soc.* **35**, 576 (1939); **36**, 619 (1940).