

interval 46.9–90.1°, 42.9 ± 0.3 cal./mole, and the molal heat capacity of liquid carbon tetrabromide

in the interval 90.1–150°, 36.7 ± 0.5 cal./mole. BERKELEY, CALIFORNIA RECEIVED APRIL 3, 1939

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The Coefficient of Expansibility of Aqueous Solutions of Urea at 27.5° Calculated from the Densities at 25 and 30°

BY FRANK T. GUCKER, JR., AND CHARLES E. MOSER

Several years ago, it was shown¹ that the apparent molal expansibility of electrolytes, like the apparent molal volume and several other properties, is a linear function of the square root of the volume concentration (molarity) and therefore that the coefficient of thermal expansibility can be expressed by an equation of the type suggested by Root.² In the course of the investigation of the properties of non-electrolytes, we published recently a precise determination of the densities of aqueous solutions of urea at 25 and 30°.³ Up to a concentration of about 3 molar, the apparent molal volume of this solute is a linear function of the *first power* of the molarity, within a few parts per million in the density. These data suffice to determine the apparent molal expansibility of urea, although the calculations are complicated by the fact that the molarity, as well as the density, is a function of the temperature. The method described below is an extension of our previous treatment of partial molal solute quantities which are functions of the molarity.⁴

The Coefficient of Expansibility.—This may be defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,m} = - \frac{1}{d} \left(\frac{\partial d}{\partial T} \right)_{P,m} \quad (1)$$

where P is the pressure and m the molality. When the apparent molal volume is a linear function of the molarity in dilute solutions, the density may be expressed by means of a power series in c

$$d = d_1 + A_1c + A_2c^2 + A_3c^3 + \dots \quad (2)$$

where d_1 is the density of the pure solvent, c is the concentration of the solute in moles per liter, and A_1 , etc., are constants characteristic of the solute and temperature. Equation (2) may be differentiated with respect to T , keeping P and m constant. Remembering that c is a function of T and that $\partial c/\partial T = -\alpha c$, the result is

(1) Gucker, *THIS JOURNAL*, **56**, 1017 (1934).

(2) Root, *ibid.*, **55**, 850 (1933).

(3) Gucker, Gage and Moser, *ibid.*, **60**, 2582 (1938).

(4) Gucker, *J. Phys. Chem.*, **38**, 307 (1934).

$$\left(\frac{\partial d}{\partial T} \right)_{P,m} = \frac{\partial d_1}{\partial T} + \left[\frac{\partial A_1}{\partial T} - A_1\alpha \right] c + \left[\frac{\partial A_2}{\partial T} - 2A_2\alpha \right] c^2 + \left[\frac{\partial A_3}{\partial T} - 3A_3\alpha \right] c^3 + \dots \quad (3)$$

If α , like d , can be expressed as a power series

$$\alpha = \alpha_1 + B_1c + B_2c^2 + B_3c^3 + \dots \quad (4)$$

we can rearrange (3) into the form

$$\left(\frac{\partial d}{\partial T} \right)_{P,m} = \frac{\partial d_1}{\partial T} + \left[\frac{\partial A_1}{\partial T} - A_1\alpha_1 \right] c + \left[\frac{\partial A_2}{\partial T} - 2A_2\alpha_1 - A_1B_1 \right] c^2 + \left[\frac{\partial A_3}{\partial T} - 3A_3\alpha_1 - 2A_2B_1 - A_1B_2 \right] c^3 \dots \quad (5)$$

Division of (5) by (2) gives at once the coefficient of expansibility as

$$\alpha = \alpha_1 - \frac{1}{d_1} \left(\frac{\partial A_1}{\partial T} \right) c - \frac{1}{d_1} \left[\frac{\partial A_2}{\partial T} - A_2\alpha_1 \right] c^2 - \frac{1}{d_1} \left[\frac{\partial A_3}{\partial T} - 2A_3\alpha_1 + 2 \frac{A_2}{d_1} \left(\frac{\partial A_1}{\partial T} \right) \right] c^3 + \dots \quad (6)$$

This equation now may be employed to calculate the coefficient of expansibility of aqueous solutions of urea at 27.5°.

The equations for the densities at 25 and 30° are³

$$d_{30} = 0.995673 + 0.015705c - 1.082 \times 10^{-4}c^2 \quad (7)$$

$$d_{25} = 0.997074 + 0.015964c - 1.315 \times 10^{-4}c^2 \quad (8)$$

Subtracting the coefficients of (8) from those of (7) and dividing by 5 gives

$$\Delta d_1/\Delta T = -280.2 \times 10^{-6}; \text{ whence } \alpha_1 = 281.2 \times 10^{-6}$$

$$\Delta A_1/\Delta T = -51.8 \times 10^{-6} \text{ and } \Delta A_2/\Delta T = 4.66 \times 10^{-6}$$

Taking the mean of the coefficients of (7) and (8) gives for the density of urea solutions at 27.5° the equation

$$d_{27.5} = 0.996374 + 0.015835c - 1.199 \times 10^{-4}c^2 \quad (9)$$

Hence, $B_1 = 0.015835$ and $B_2 = 1.199 \times 10^{-4}$. Substituting these values into (5) gives for the mean coefficient of expansibility the equation

$$\alpha_{27.5} = (281.2 + 52.0c - 4.71c^2) \times 10^{-6} \quad (10)$$

Terms involving higher powers of c are negligible at the highest concentrations to which equations (7) and (8) are applicable. The estimated un-

certainty of equation (10) is $\pm 0.5\%$ in a 3 molar solution. The uncertainty decreases considerably as we approach pure water.

Apparent and Partial Molal Expansibilities.—The apparent molal expansibility has been defined¹ like the apparent molal volume as

$$\Phi E_2 = \alpha V - \alpha_1 V_1 \quad (11)$$

where V is the number of ml. of solution which contains one mole of solute, and V_1 is the volume of solvent used in making the solution. The apparent molal expansibility is the temperature derivative of the apparent molal volume. A more convenient equation for calculating the apparent molal expansibility¹ is

$$\Phi E_2 = \frac{1000}{c} (\alpha - \alpha_1) + \alpha_1 \Phi V_2 \quad (12)$$

The mean of the values³ at 25 and 30° gives for the apparent molal volume at 27.5°

$$\Phi V_2 = 44.385 + 0.1203c \quad (13)$$

Substituting the coefficients from (10) and (13) gives the apparent molal expansibility as

$$\Phi E_2 = 0.0645 - 0.00468c \quad (14)$$

The partial molal expansibilities of solute and solvent, which are the temperature coefficients of the corresponding partial molal volumes, may be calculated conveniently from the equations for the apparent molal expansibility and volume by means of formulas already derived^{3,4} or closely analogous to them. For numerical calculations they may be put in the form

$$\begin{aligned} \bar{E}_2 &= 0.0645 - 0.00936c + 0.00208c^2 \\ \bar{E}_1 &= 0.00508c + 0.0000846c^2 - 1 \times 10^{-8}c^4 \end{aligned}$$

Discussion.—We have shown previously³ that the apparent molal volume of urea is very nearly the same as the molal volume of the solid, and that it changes between 0 and 1 molar only about 4% as much as a typical 1-1 electrolyte. It is rather surprising to find that its apparent molal expansibility is much larger in proportion. The limiting value at zero concentration is about that of a typical 1-1 electrolyte and the change between 0 and 1 molar is about a quarter as great as for such a polar compound. Thus we see that, although the solute-solvent forces are much less in solutions of urea than in electrolytic ones, the temperature coefficient is much more nearly the same in the two different environments. In the case of the volume properties, at least, we have shown a definite linearity with the first power of the concentration in the case of urea, which differentiates it clearly from electrolytes.

Summary

We have developed a method of calculating the coefficient of expansibility of any solution for which the density is known as a function of the molarity at two different temperatures. We have applied the method to urea solutions at 27.5° and give equations for the coefficient of expansibility, apparent and partial molal expansibilities. The apparent molal expansibility of urea is about as great as that of a 1-1 electrolyte, although it is a linear function of the first power and not the square root of the molarity.

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The Addition of Hydrogen Halides to *cis*- and *trans*-2-Pentene

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Introduction

Over ten years have elapsed since Kharasch and Darkis² published their interpretation of the addition of hydrogen bromide to 2-pentene. At that time, and for some time thereafter, the results of various workers²⁻⁴ seemed to indicate different ratios of products depending upon the conditions of addition and the source and previous

treatment of the pentene employed. To account for this phenomenon, Kharasch and Darkis² postulated the existence of two isomeric 2-pentenes (electromers) differing in their electronic configurations, of which one added hydrogen bromide to give 2-bromopentane, and the other, 3-bromopentane.

More recently the matter has been investigated by Lauer and Stodola⁵ and Lucas and Prater.⁶ The latter authors isolated the *cis* and *trans* isomers of 2-pentene, and claim, on the

(1) Du Pont Fellow, 1938-1939.
 (2) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928).
 (3) Lucas and Moyses, *THIS JOURNAL*, **47**, 1459 (1925); Lucas, Simpson, and Carter, *ibid.*, **47**, 1462 (1925).
 (4) Sherrill, Otto, and Pickett, *ibid.*, **51**, 3023 (1929); Sherrill, Baldwin, and Haas, *ibid.*, **51**, 3034 (1929).

(5) Lauer and Stodola, *ibid.*, **56**, 1216 (1934).
 (6) Lucas and Prater, *ibid.*, **59**, 1682 (1937).