NOTES.

Estimation of Deuterium Oxide–Water Mixtures. By William H. Patterson.

In many experiments with heavy water a rapid method of estimating the D_2O content by using only small quantities is desirable. With this in view, critical and mutual solubility methods were tested, correlated with direct determination of density.

A mixture of ethyl alcohol and ordinary paraffin (*n*-decane) has a *C.S.T.* a little above room temperature and is very sensitive to traces of water, 1 mg. of which raises the *C.S.T.* of a mixture of 0·5 g. of each of the organic liquids by 1·7°. The effect of D_2O, however, was nearly the same (slightly lower), no doubt owing to rapid exchange.

The following results relate only to the system D_2O–H_2O–phenol, for which constant results were found unchanged after several days. Timmermans and Poppe (*Compt. rend.*, 1935, **201**, 524) gave 12·25° as the rise of *C.S.T.* when D_2O replaces H_2O, and Hall, Wentzel, and Smith (*J. Amer. Chem. Soc.*, 1934, **56**, 1822) found a 5·58° rise on using water with 47·2% D_2O content ($N = 0{\cdot}466$). The choice of the actual temperature of mutual miscibility is to some extent arbitrary. When concentrations near to the critical are tried (giving the *C.S.T.*), a range of opalescence of nearly 3° is found; 10% change of phenol content on either side reduces this to 0·5°. In all cases, however, the advent of turbidity or opaqueness is sharp and definite, and when this is used as standard the *C.S.T.* of water–phenol is 66·0° and no change can be noted with variations in phenol content between 34·2 and 37·8% (Carrington, Hickson, and Patterson, J., 1925, **127**, 2544).

A pyknometer was used for density determinations, made by blowing a bulb on a tube and drawing the ends into capillaries to give a **V**-shape. Since an ordinary balance was used for weighing, the pyknometer was made to have a volume of 0·4882 c.c., and measurements with it were found to be as accurate as allowed by possible errors in weighing (0·1—0·2 mg.). For similar reasons a few cg. were taken in the miscibility tests. Use of a micro-balance would probably increase accuracy even with smaller samples.

Mixtures were made by diluting the original sample, stated to be 99·6% D_2O, $d_{4^\circ}^{20^\circ}$ 1·10495 (Found: 1·1043, after the tube had been opened several times). Since the nature of the curves had first to be studied, no attempt was made to measure temperature differences below 0·05°. The following results were obtained :

(1) D_2O 99·6% ($N = 0{\cdot}996$), $d_{4^\circ}^{20^\circ}$ 1·1043.

PhOH, % ...	50·1	45·2	38·5	36·3	33·9	26·3	24·9	24·1	23·1	22·0	19·6
M.M.T.	74·10°	76·35°	77·75°	78·00°	78·15°	77·95°	77·95°	77·75°	77·75°	77·3°	76·25°

Max.: 78·2°; phenol, 31%.

(2) D_2O 66·76% (N = 0·644), $d_{4°}^{20°}$ 1·0678.

PhOH, %	49·6	47·3	37·3	30·2	28·2	24·9
M.M.T.	70·30°	72·30°	74·25°	74·40°	74·2°	74·0°

Max.: 74·40°; phenol, 32·5%.

(3) D_2O 52·65% (N = 0·500), $d_{4°}^{20°}$ 1·0506.

PhOH, %	50·4	44·0	35·7	30·9	28·1	23·1	21·5	16·5
M.M.T.	67·30°	71·15°	72·35°	72·20°	71·90°	71·25°	70·70°	67·30°

Max.: 72·20°; phenol, 33%.

(4) D_2O 19·53% (N = 0·179), $d_{4°}^{20°}$ 1·0170.

PhOH, %	48·8	41·6	36·4	25·9	19·3
M.M.T.	66·2°	68·05°	68·55°	68·05°	65·5°

Max.: 68·6°; phenol, 35%.

The figures show that densities have a slight negative deviation from linear. The critical concentration of the phenol changes progressively from 36·1% with H_2O to 31·0% for D_2O. Otherwise the curves are similar and enable concentrations other than critical to be used for estimation.

The temperature rise in replacing H_2O by alleged 99·6% D_2O and by 52·65% D_2O is 12·2° and 6·2° respectively. The latter mixture is equimolar (N = 0·5), so a rise of 1·24° represents 0·1 mol. fraction of D_2O. This figure enables an approximate analysis to be made. For intermediate concentrations slight increase is necessary: the figure calculated from the results of Hall, Wentzel, and Smith (*loc. cit.*) is 1·25°.

This variation, which needs more accurate determination if results correct to 1% are required, is probably due to the fact that only three curves are concerned with two-component systems, *i.e.*, phenol and 100% D_2O, 52·65% D_2O (corresponding to HDO), or 100% H_2O: all other curves represent three-component systems.—QUEEN MARY COLLEGE, UNIVERSITY OF LONDON. [*Received, August 25th*, 1937.]

The Preparation of 2 : 4-Dinitrobenzonitrile and 2 : 4-Dinitrobenzoic Acid.

By FREDERICK R. STORRIE.

THE Curtius–Bollenbach method of preparing 2 : 4-dinitrobenzoic acid (*J. pr. Chem.*, 1907, **76**, 287) by the chromic anhydride oxidation of 2 : 4-dinitrotoluene in sulphuric acid is not satisfactory (cf. Borsche and Butschli, *Annalen*, 1936, **522**, 285).

We have prepared 2 : 4-dinitrobenzonitrile by diazotising 2 : 4-dinitroaniline by Hodgson and Walker's method (J., 1933, 1620), using potassium nickelocyanide (Korczyński, Mroziński, and Villau, *Compt. rend.*, 1920, **171**, 183) instead of the cuprocyanide (which gives less than a 60% yield of a very impure nitrile), and having the reaction mixture neutral (cf. "Organic Syntheses," IV, 70). The hydrolysis of the nitrile to the amide, and the conversion of the latter into the acid by means of nitrous acid, can be accomplished without isolation of the amide.

A filtered solution of 2 : 4-dinitrobenzenediazonium sulphate (prepared by Hodgson and Walker's method from 18·3 g. of 2 : 4-dinitroaniline in 175 c.c. of glacial acetic acid, and 7·7 g. of sodium nitrite in 55 c.c. of concentrated sulphuric acid) was added slowly with stirring to a cooled solution of potassium nickelocyanide (prepared from 35 g. of potassium cyanide in 150 c.c. of water, and 16·5 g. of nickel chloride, or 30 g. of nickel sulphate, in 50 c.c. of water) containing 300 c.c. of water and 150 g. of anhydrous sodium carbonate. During the addition a further 300 c.c. of water and sodium carbonate (about 50 g.) were added until the reaction mixture was neutral, and the temperature was allowed to rise to 30—35°. The mixture was stirred at 90° for ½ hour and cooled and the solid separated by filtration was washed with warm water, then with sodium hydroxide solution and water, dried, refluxed with light petroleum (b. p. 60—80°—to remove any *m*-dinitrobenzene), and crystallised from alcohol, giving 2 : 4-dinitrobenzonitrile, m. p. 103—104° (Friedländer and Cohn, *Sitz. Wien. Akad.*, 1902, **111**, 437, give m. p. 103—104°), in 85% yield.

2 : 4-Dinitrobenzonitrile (4 g.), water (6 c.c.), and concentrated sulphuric acid (12 c.c.) were refluxed for ½ hour, water (6 c.c.) added, and the suspension stirred while a solution of sodium nitrite (1 g.) was run in. The cooled liquid was filtered and extracted with ether. The extract was shaken with sodium carbonate solution, which was then used to dissolve the filtered acid. Acidification of the sodium salt solution gave 2 : 4-dinitrobenzoic acid, m. p. 179—180° (Curtius and Bollenbach give m. p. 180°), in 95% yield.

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