equivalent quantity of thiosulfate (10.2 cc.) and finally, with constant stirring, 50 cc. of hydrochloric acid (2 *N*). The solution acquires at once the color of bichromate; then, after a lapse of several seconds, instantly that of iodized starch. This second color fades very slowly; after six minutes it is still very pronounced; it requires about twelve minutes to disappear completely. During the whole of this period the presence of thiosulfate in the solution can be verified by its reaction on sodium azide.

Summary

The excess of thiosulfate used in the iodimetric titration of chromate in feebly acid solution is attributed to the formation of a complex chromic thiosulfate during the reduction of the chromate. This complex reacts slowly with free iodine.

LABORATOIRE DE CHIMIE GÉNÉRALE
À LA SORBONNE
PARIS, FRANCE

RECEIVED DECEMBER 10, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Tertiary Butyl Alcohol as a Solvent for Cryoscopic Molecular Weight Determinations

BY GEORGE S. PARKS, GRANT E. WARREN AND EARNEST S. GREENE

This investigation was carried out a few years ago to determine the suitability of tertiary butyl alcohol as a solvent for molecular weight determinations by the Beckmann freezing point method. As this alcohol can now be produced cheaply and in a very pure form as a by-product of oil cracking processes by several companies in the United States, the publication of our results appears to be timely.

The principal earlier investigation on the subject is that of Atkins,[1] whose alcohol was probably much less pure than the material now available. At any rate his results, with *p*-dibromobenzene, acetanilide, thiocarbamide, *p*-toluidine and α-naphthylamine as solutes, did not appear very satisfactory and the values thereby obtained for the cryoscopic constant of *t*-butyl alcohol varied from 7.3 to 15.4. To explain his rather erratic data Atkins suggested that the butyl alcohol probably exists in two crystalline modifications, one of which may be very unstable with a heat of fusion of about 13.8 calories per gram. In our present study we also made measurements with acetanilide and *p*-toluidine but failed to obtain the highly abnormal results reported in this earlier investigation.

Method and Apparatus

The Beckmann freezing point method, as described in standard laboratory manuals such as those of Findlay[2] and Daniels, Mathews and Williams,[3] was used in all our molecular weight determinations. Of course, the hygroscopic character of the solvent and its rather pronounced tendency to undercool before crystallization had to be taken into consideration in the experimental procedure. In order to prevent entrance of moisture from the air, the inner freezing tube was equipped with tightly fitting rubber stoppers and the wire stirrer was operated within a sleeve of thin, flexible rubber, which thus made an air-tight seal. To avoid an excessive amount of undercooling of the entire butyl alcohol solution, a small piece of platinum wire was fused through the bottom of this inner tube. During a determination crystallization could then be started at any desired degree of undercooling by removing the tube and touching the external portion of this wire for an instant to a soldering copper which had been previously chilled in ice or solid carbon dioxide. A three-liter Dewar jar, filled with water which was kept about 1.5° below the freezing point of the alcohol solutions, served as the external cooling bath.

The freezing point depressions for the molecular weight determinations were always measured with a Beckmann thermometer which had been previously calibrated by the U. S. Bureau of Standards. Other temperature measurements, including the melting point of the purified *t*-butyl alcohol and the freezing points in our study of the *t*-butyl-*t*-amyl alcohol system, were made with a similarly calibrated mercury thermometer which could be read to ±0.04°.

Materials

Several liters of *t*-butyl alcohol, m. p. about 20°, were generously given to us for this investigation by the Standard Oil Development Company. This material was first dehydrated by two fractional distillations over lime and was then subjected to ten fractional crystallizations. About two liters of final product, melting at 25.4°, was thus obtained.

The various solutes employed in this investigation were for the most part samples of the substances which have have been previously used in specific heat studies at Stanford University. Details concerning the preparation of the methyl, ethyl, *n*-propyl, isopropyl and *t*-amyl alcohols, *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane, *o*-xylene, *m*-xylene, *p*-xylene, *n*- and *t*-butylbenzenes, ethyl benzene, *p*-cymene, diphenylmethane, acetic acid, acetone and phenol have been given in

---

[1] Atkins, *J. Chem. Soc.*, **99**, 10 (1911).

[2] Findlay, "Practical Physical Chemistry," Longmans, Green and Co., London, 1931, p. 119.

[3] Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1934, p. 61.

other places.[4] The ethyl acetate, *p*-toluidine and acetanilide were C. P. Eastman products. The carbon tetrachloride was a specially pure Kahlbaum material. The water was twice distilled. The secondary butyl alcohol and the methylbutylcarbinol were kindly prepared for us in very pure form by H. E. Buc of the Standard Oil Development Company.

Evaluation of the Cryoscopic Constant

The calculations of molecular weights throughout this paper have been made with the equation

$$M = 1000\ K(g/G\ \Delta T_f) \qquad (1)$$

where M is the molecular weight of the solute, K the cryoscopic constant for the solvent, g the number of grams of solute in the solution, G the number of grams of solvent and ΔT_f the difference between the original freezing point (25.4°) of the *t*-butyl alcohol and that of the particular solution involved. This equation is strictly valid for only extremely dilute solutions in which also the partial vapor pressures conform to the requirements of Raoult's law and from which crystals of the pure solvent separate out on freezing. However, in the present case, if the requirements of Raoult's law and pure crystal formation are met satisfactorily, the approximations used in its derivation should not involve us in any error over 1.0% for solutions with freezing point depressions as great as 2.0° when the value for K at infinite dilution is employed. Moreover, by employing a value for K which is exactly applicable in Equation 1 when ΔT_f is 1°, the error in using this approximate equation for "perfect" (*i. e.*, conformable to Raoult's law) solutions up to depressions of 2° can be kept under 0.5%.

The cryoscopic constant K can be evaluated in two ways: *viz.*, (a) by experimental measurement of the freezing point depressions for solutes of known molecular weight, which form perfect solutions with the given solvent, and (b) by use of the thermodynamic relation

$$1000\ K = RT^2/\Delta H \qquad (2)$$

where T represents the absolute temperature of the freezing point of the pure solvent and ΔH is its heat of fusion per gram. In the present study we have used both methods. De Forcrand[5] by a method of mixtures has found 20.98 calories per gram for the heat of fusion of *t*-butyl alcohol, while Parks and Anderson[6] using the Nernst calorimetric procedure have obtained 21.88 calories per gram. The first value is probably too low, but the second may be somewhat high. Accordingly, taking the mean of 21.43 calories per gram, we find K = 8.27 by Equation 2.

Using six representative solutes of exceptional purity (methyl alcohol, ethyl alcohol, *n*-heptane, cyclohexane, *p*-xylene and carbon tetrachloride), we have also measured ΔT_f for solutions of various concentrations and have thereby obtained by Equation 1 and the assumption of the theoretical molecular weight, values of K at different values of ΔT_f. In Fig. 1 these results are plotted in the cases of ethyl alcohol and carbon tetrachloride. By extrapolation of the straight lines the corresponding values of K_0 for infinitely dilute solutions can be estimated readily. In Table I are tabulated the experimental values of K at ΔT_f = 1° and this limiting K_0 for the six solutes previously mentioned.

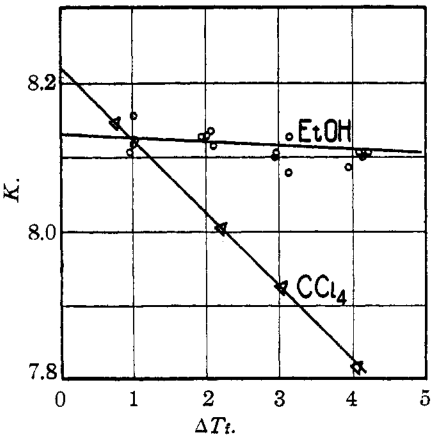

Fig. 1.—Showing the experimental values for the cryoscopic constant of *t*-butyl alcohol obtained with ethyl alcohol and carbon tetrachloride as solutes.

TABLE I

EXPERIMENTAL VALUES FOR THE CRYOSCOPIC CONSTANT OF TERTIARY BUTYL ALCOHOL

Solute	K for ΔT_f = 1°	K_0
Methyl alcohol	8.33	8.33
Ethyl alcohol	8.12	8.13
n-Heptane	8.21	8.37
Cyclohexane	8.16	8.30
p-Xylene	8.28	8.47
Carbon tetrachloride	8.11	8.22
Mean	8.20	8.30

The mean result for K_0 obtained in this manner is in excellent agreement with that just calculated

---

[4] Huffman, Parks and Barmore, THIS JOURNAL, **53**, 3877 (1931); Huffman, Parks and Daniels, *ibid.*, **52**, 1548 (1930); Parks, *ibid.*, **47**, 340 (1925); Parks and Huffman, *ibid.*, **48**, 2789 (1926), and **52**, 4382 (1930); Parks, Huffman and Barmore, *ibid.*, **55**, 2733 (1933); Parks, Huffman and Thomas, *ibid.*, **52**, 1033 (1930); and Parks and Kelley, *ibid.*, **47**, 2090 (1925).

[5] De Forcrand, *Compt. rend.*, **136**, 1034 (1903).

[6] Parks and Anderson, THIS JOURNAL, **48**, 1508 (1926).

by thermodynamics from the heat of fusion. The value for K when $\Delta T_f = 1°$ is 1.2% lower, as in all cases save that of methyl alcohol there was more or less decrease in the experimentally determined value of K with increasing ΔT_f values. For practical purposes, since most molecular weight determinations with this solvent will probably be made with freezing point depressions up to about 1° in magnitude, we now suggest a mean between these values for the zero and one degree depressions, namely, 8.25 for K.

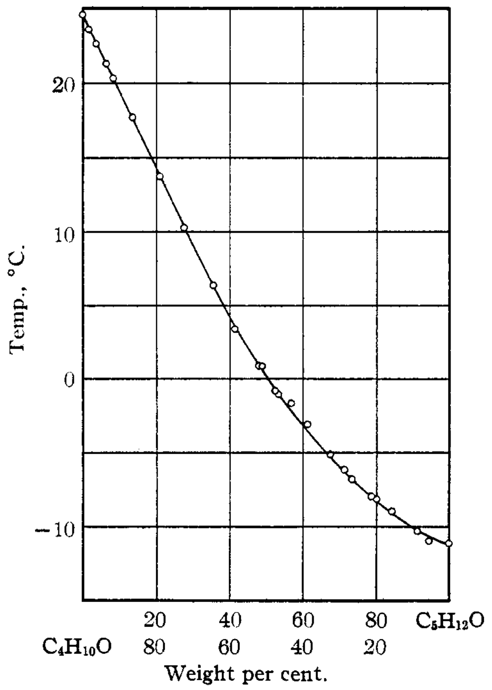

Fig. 2.—The curve for the initial freezing points of the *t*-butyl–*t*-amyl alcohol system.

Molecular Weight Results for Twenty-eight Solutes

In turn, with the evaluation of K in Equation 1 it now becomes possible to calculate the molecular weights of solutes in *t*-butyl alcohol from the observed freezing point depressions at various concentrations. This has been done for twenty-eight different solutes, including the six used in the previous section for the evaluation of the cryoscopic constant. While in all cases at least four different concentrations of a given solute were employed, a depression of about 1° is probably the optimum with this solvent, since it can be measured with a maximum error of perhaps 0.4% and at the same time such solutions are not so concentrated as to involve very marked departures from Raoult's law. The various solutes with the percentage differences between the experimentally determined molecular weight at 1° depression and the theoretical value were as follows: water, −1.0; methyl alcohol, −1.0; ethyl alcohol, +1.1; *n*-propyl alcohol, +2.7; isopropyl alcohol, +23.1; *s*-butyl alcohol, +16.5; *t*-amyl alcohol, +90.9; methylbutylcarbinol, −2.3; *n*-hexane, +2.4; *n*-heptane, +0.3; *n*-octane, −0.5; cyclohexane, +0.7; methylcyclohexane, −0.9; *o*-xylene, 0.0; *m*-xylene, −1.1; *p*-xylene, −0.5; ethylbenzene, −0.4; *p*-cymene, +0.5; *n*-butylbenzene, +0.7; *t*-butylbenzene, −0.9; diphenylmethane, +3.0; carbon tetrachlorine +1.3; acetic acid, −3.9; acetone, −0.5; ethyl acetate, −2.0; phenol, −3.7; *p*-toluidine, −4.7; and acetanilide, +1.2.

These results are at least reasonably satisfactory for all the solutes employed save the three alcohols, isopropyl, secondary butyl and *t*-amyl and perhaps *p*-toluidine. However, our experimental value of 102.1 for this last compound is much closer to the theoretical (107.1) than the results of 61.4 to 65.8 obtained previously by Atkins;[1] and possibly some of the discrepancy found here is due to impurities in our sample of *p*-toluidine, since this was one of the least pure of our materials. Incidentally, in the case of phenol the somewhat low result may be partially due to compound formation with the solvent. An earlier study of the *t*-butyl alcohol–phenol system by Paternò and Ampola[7] has given indications of the existence of the solid compound $3(CH_3)_3COH–C_6H_5OH$ and a recalculation of our data on the assumption that this compound also persists in the liquid phase and thereby reduces the effective amount of solvent present yields 93.7 for the molecular weight of phenol as against 94.05 for the formula value.

With the two secondary alcohols and the *t*-amyl alcohol association might at first be suggested as an explanation for our very high results. However, some preliminary freezing point tests on the crystalline material separating out from such solutions indicated that mixed crystals were being formed. This hypothesis was then verified in the case of *t*-amyl alcohol by the investigation described in the next section.

The System *t*-Butyl Alcohol–*t*-Amyl Alcohol

Twenty-four solutions containing *t*-butyl and *t*-amyl alcohols in various proportions were made

---

(7) Paternò and Ampola, *Gazz. chim. ital.*, **27**, 481 (1897).

up. The samples of the alcohols employed for this purpose melted at 24.6° and −11.1°, respectively, the butyl alcohol being a reserve material which was somewhat less pure than that used in the preceding molecular weight determinations. The freezing points of these solutions were then measured and found to be in all cases intermediate between those of the two alcohols. The results can be seen plotted in Fig. 2. They lie very consistently upon a curve which is typical of a system that forms mixed crystals on freezing. There is no indication of a eutectic point, such as would be necessary if pure crystals of the two components were separating out.

Of course, the application of Equation 1 to such a system, in which mixed crystals are formed on freezing, is not legitimate, and this fact explains our erratic molecular weight results for *t*-amyl alcohol and also, in all probability, for the propyl and butyl secondary alcohols.

Summary

The suitability of tertiary butyl alcohol as a solvent for molecular weight determinations by the freezing point method has been studied. From thermodynamic data and from the freezing point depressions of solutions of six typical solutes a value of 8.25 has been suggested for the cryoscopic constant. The molecular weights of twenty-eight compounds dissolved in tertiary butyl alcohol have then been determined. The results indicate that this solvent is satisfactory in cryoscopic determinations for most types of organic compounds, including primary alcohols and all classes of hydrocarbons. However, it cannot be used when certain closely related secondary and tertiary alcohols are the solutes because of the formation of mixed crystals on freezing.

STANFORD UNIVERSITY, CALIF.

RECEIVED DECEMBER 17, 1934

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Estimation of Iron in the Presence of Titanium: An Aeration Process[1,2]

BY WILLIAM M. THORNTON, JR., AND REUBEN ROSEMAN[3]

A number of years ago Gooch and Newton[4] published an interesting volumetric process for estimating iron in the presence of titanium. This method depends upon the fact that, if to a sulfuric acid solution containing bivalent iron and trivalent titanium solid bismuth trioxide be added, the titanium is completely oxidized to the quadrivalent state while the ferrous iron is not appreciably affected. After filtration from the surplus bismuth oxide and the precipitated bismuth, the iron can be titrated with a standard solution of potassium permanganate.

Now it is known that sulfuric acid solutions of ferrous sulfate undergo atmospheric oxidation but very slowly at room temperatures.[5] Thus, Baskerville and Stevenson[5] found that on passing air for twelve hours through a solution of Mohr's salt, acidulated with sulfuric acid, there resulted only 0.0001 g. of Fe^{+++} out of a total of approximately 0.71 g. of Fe^{++}. On the other hand, titanous sulfate solutions of ordinary acidity are extremely unstable in air. Accordingly, while reduction of titanium in the Jones reductor proceeds quantitatively to the trivalent condition, the deoxidized substance is usually collected under a protective solution (ferric sulfate), whereby the titanium is converted immediately to the quadrivalent state with the formation of an equivalent amount of the more stable ferrous sulfate.[6]

This greater stability toward atmospheric oxidation on the part of ferrous sulfate suggested the possibility of estimating Fe^{++} in the presence of Ti^{+++} by subjecting the solution containing these ions to an air-bubbling process. It was hoped that in the time required to effect the complete

---

[1] From Ph.D. dissertation of Reuben Roseman, Johns Hopkins University, June, 1933.

[2] For a preliminary report of this work see Thornton, Roseman and Katzoff, THIS JOURNAL, **54**, 2131 (1932).

[3] Holder of the J. T. Baker Chemical Company Research Fellowship in Analytical Chemistry (Eastern Division), 1930–1931.

[4] Gooch and Newton, *Am. J. Sci.*, [4] **23**, 365 (1907).

[5] See, for example, McBain, *J. Phys. Chem.*, **5**, 623 (1901); Peters and Moody, *Am. J. Sci.*, [4] **12**, 369 (1901); Varinskii and Laska, *Ann. chim. anal. appl.*, **14**, 45 (1909); Baskerville and Stevenson, THIS JOURNAL, **33**, 1104 (1911); Hillebrand, U. S. Geol. Survey, *Bull.* **700**, 199 (1919); Jilek, *Chem. Listy*, **15**, 105, 138 (1921); Banerjee, *Z. anorg. allgem. Chem.*, **128**, 343 (1923); Posnjak, *Am. Inst. Mining Met. Eng.*, No. **1615D** (1926); Friend and Pritchett, *J. Chem. Soc.*, 3227 (1928); Lamb and Elder, THIS JOURNAL, **53**, 137 (1931); Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley & Sons, Inc., New York, 1931, p. 115.

[6] Lundell and Knowles, THIS JOURNAL, **45**, 2620 (1923); *Ind. Eng. Chem.*, **16**, 723 (1924). *Cf.* Newton, *Am. J. Sci.*, [4] **25**, 130 (1908).