pounds. Several years ago we published[1] data for the heats of reaction of sodium and potassium with water, from which the heats of formation of the hydroxide could readily have been calculated. Being interested in the other aspects of the data we did not make this simple calculation and furthermore failed[2] to label our data sufficiently well to enable other interested individuals to utilize the results in making this or other calculations. The purpose of this note is to clarify the labeling of our earlier results and to use them to compute the heats of formation of NaOH and KOH at infinite dilution in water at 25°.

For the reaction[3] metal(s) + $\infty H_2O(l) \rightarrow$ metallic hydroxide (∞H_2O) + $^1/_2H_2(g)$, $\Delta E_{298.16} = -44{,}350$ and $-47{,}190$ cal. for sodium[4] and potassium, respectively. These are the means of the experimental quantities, a constant volume calorimeter having been used.[1] Correcting to constant pressure and using $-68{,}317$ cal. as the standard heat of formation of water[5] at 25°

$$Na(s) + {}^1/_2H_2(g) + {}^1/_2O_2(g) + \infty H_2O(l) \longrightarrow NaOH(\infty H_2O) \quad \Delta H_{298.16} = -112.37 \text{ kcal.};$$

$$K(s) + {}^1/_2H_2(g) + {}^1/_2O_2(g) + \infty H_2O(l) \longrightarrow KOH(\infty H_2O) \quad \Delta H_{298.16} = -115.21 \text{ kcal.}$$

The corresponding data given in the National Bureau of Standards compilation[5] are -112.23 kcal. for sodium and -115.00 kcal. for potassium.

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(1) E. E. Ketchen and W. E. Wallace, THIS JOURNAL, **73**, 5810 (1951).

(2) We are grateful to Professor Leo Brewer of the University of California for calling attention to this.

(3) Corrections to infinite dilution were made using data published by J. H. Sturtevant, THIS JOURNAL, **62**, 2276 (1940) for sodium hydroxide and by H. S. Harned and M. S. Cook, *ibid*, **59**, 496 (1937) for potassium hydroxide.

(4) In reference (1) Table I contains a typographical error. One of the individual heats of reaction of sodium with water reads −44,400 cal. instead of the correct value −44,460 cal.

(5) "Selected Values of Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office. Washington, D. C., 1952,

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The Behavior of 1,2-Diketones at the Dropping Mercury Electrode: an Addendum

BY NELSON J. LEONARD, H. A. LAITINEN AND EDWARD H. MOTTUS

RECEIVED MAY 12, 1954

In the paper by Schwabe and Berg,[1] which reached us after the publication of our article[2] on the polarographic reduction of 1,2-diketones,[3] the reduction of camphorquinone was described as a two-electron process. Since our conclusion that the reduction involved a one electron process was based in part upon the favorable comparison of calculated (for camphorquinone in 50% isopropyl alcohol–water) and observed (for camphor in 96% ethyl alcohol–water)[4] diffusion coefficients, it seemed desirable to examine more critically the basis of this comparison. The viscosity of isopropyl alcohol–water mixtures passes through a maximum[5] near the 50% composition which was used as the solvent in our experiments and thus chances to be more than twice that of 96% ethanol and about three times that of water. A comparison[6] of the polarographic wave heights of camphorquinone in water and in 50% isopropyl alcohol–water led to reasonable values of a diffusion coefficient only if n were taken equal to 2. In water, if n were assumed equal to 1, an improbably high value (34×10^{-6} cm.^{2}/sec.) was obtained.

Apparently, therefore, the reduction of camphorquinone is a two electron process,[1] and presumably this is so for the other members of the series of 1,2-diketones[2,7] which were found to be reducible at the dropping mercury electrode.[8] This conclusion does not affect the half-wave potentials as reported in our previous paper and therefore does not alter the order of reducibility of the 1,2-diketones. It will be noted that Schwabe and Berg[1] proposed a mechanism for the initial reduction step identical with that which we suggested.[9] The preferred fate of the intermediate radical, if such is indeed formed, would then require rapid absorption of the second electron and proton. It remains true that any mechanistic sequence proposed for the polarographic reduction must take into account the steric factors[2] in the acyclic and cyclic 1,2-dicarbonyl systems.

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(1) K. Schwabe and H. Berg, *Z. Elektrochem.*, **56**, 952 (1952).

(2) N. J. Leonard, H. A. Laitinen and E. H. Mottus, THIS JOURNAL, **75**, 3300 (1953).

(3) See also S. Wawzonek, *Anal. Chem.*, **26**, 65 (1954).

(4) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., Vol. 5, 1929, p. 74.

(5) J. Traube, *Ber.*, **19**, 871 (1886), found the following viscosities: at 20°, 10% (wt. % *i*-PrOH in H_2O), 16.10; 50%, 38.17; 100%, 25.43; at 30°, 10%, 12.30; 50%, 25.58; 100%, 18.78 millipoises.

(6) Experiments by Mr. R. A. Osteryoung in this Laboratory.

(7) See also R. Pleticha, *Chem. Listy*, **46**, 69 (1952); *ibid.*, **47**, 43 (1953).

(8) Examination of other polarographic data accumulated in this Laboratory in July, 1950, when some of our early measurements were made, cast doubt upon the calibration of the recorder as to current sensitivity. In particular, this affected the value of camphorquinone in the same direction as did the viscosity.

(9) Figure 1D, in ref. 2.

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Regularities in the Densities of Dilute Solutions of Some Monochlorobenzotrihalides[1]

BY RICHARD H. MYERS, MARCUS E. HOBBS AND PAUL M. GROSS

RECEIVED APRIL 12, 1954

In the measurement of the electric moments of some monochlorobenzotrihalides, using dilute benzene solutions, certain regularities were noted in the ratio, $\Delta d/f_2$, of the density increment to the mole fraction of the solute. Since these regularities may be of significance in similar or other related investigations the results of the density determinations are reported below.

Experimental

The physical constants determined for the several compounds used in the investigation are given in Table I where $d^{30}{}_4$ is the density, $n^{30}{}_D$ the refractive index, f.p. the freezing

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(1) Taken in part from the Ph.D. Thesis of Richard H. Myers, Duke University.

TABLE I

Substance	d^{30}_4 (g./ml.)	n^{30}_D	F.p., °C.	D.R., °C.
Benzene	0.86853	....	....	80.06
Chlorobenzene	1.0960	1.5192	....	131.6_5–131.66
p-Dichlorobenzene	-s-	1.533 (m.p.)	53.29 ± 0.02	.....
Benzotrifluoride	1.1745	1.4100	−29.07 ± .02	101.9_6
o-Chlorobenzotrifluoride	1.3563	1.4517	6.39 ± .02	152.2_2–152.2_8
m-Chlorobenzotrifluoride	1.3293	1.4420	56.49 ± .02	137.6_0–137.6_7
p-Chlorobenzotrifluoride	1.3276	1.4420	−33.18 ± .08	138.5_6–138.5_8
Benzotrichloride	1.3624	1.3624	− 4.55 ± .02	106.7–106.9 (20 mm.)
o-Chlorobenzotrichloride	1.5080	1.5791	28.56 ± .02	113.8–114.1 (5.5 mm.)
m-Chlorobenzotrichloride	1.4760	1.5671	0.61 ± .02	114.8–114.9 (6.4 mm.)
p-Chlorobenzotrichloride	1.4733	1.5684	5.82 ± .02	106.3–106.7 (6.0 mm.)
Benzotribromide	-s-	1.639 (m.p.)	57.1 ± .4 (m.p.)	.....
o-Chlorobenzotribromide	2.2610	1.6630	29.9 ± .3 (m.p.)	141.0–141.5 (1 mm.)
m-Chlorobenzotribromide	2.2141	1.6495	3.5 ± .5 (m.p.)	99–101 (1 mm.)
p-Chlorobenzotribromide	-s-	1.652 (m.p.)	46.1 ± .2 (m.p.)	124–126 (1 mm.)

point unless otherwise noted and D.R. the distilling range at 760 mm. unless otherwise specified.

The constants reported in Table I compare favorably with the recent values found in the literature although the latter are somewhat limited in number. The purification and preparation procedures of the various compounds followed the usual lines except for *o*-chlorobenzotribromide which was prepared by Mr. J. B. Bond in this Laboratory using a modification of a halogen replacement reaction reported by Henne and Newman.[2] By slow addition with vigorous stirring of 250 ml. of CS_2 containing 0.28 mole of $AlBr_3$ to 300 ml. of CS_2 containing 0.27 mole of *o*-chlorobenzotrifluoride, a product was prepared, the middle fraction of which, in a reduced pressure distillation, amounted to 65.9 g.

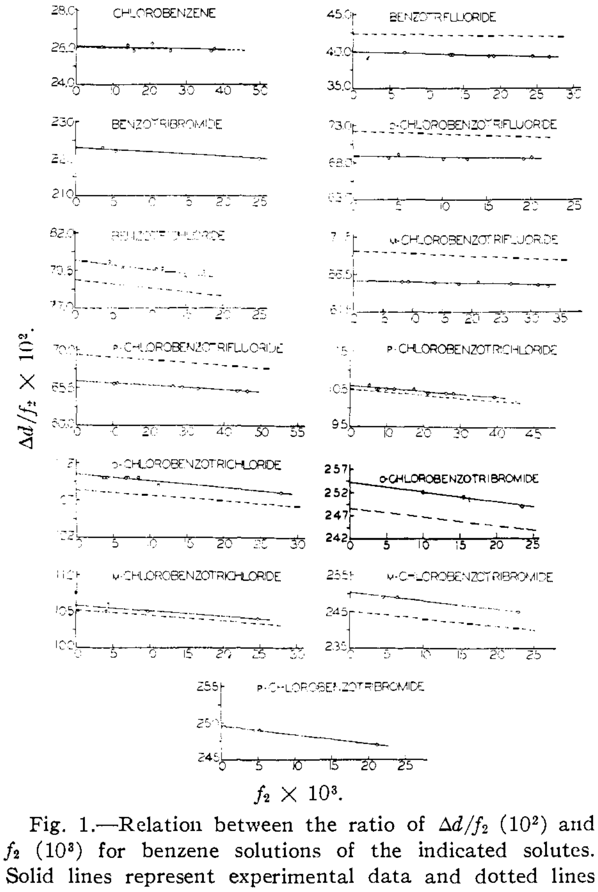

Fig. 1.—Relation between the ratio of $\Delta d/f_2$ (10^2) and f_2 (10^3) for benzene solutions of the indicated solutes. Solid lines represent experimental data and dotted lines the ideal values.

Subsequent fractional distillation at reduced pressure, 141–142° (1 mm.), yielded a product having a cryoscopic molecular weight of 357 compared to the calculated value of 363.3. *Anal.* Calcd.: C, 23.14; halogen, 75.75. Found: C, 23.24; halogen, 76.21. The halogen was calculated on the basis of one atom of chlorine to three atoms of bromine. Because of uncertainties in or lack of physical constants from the literature, benzotribromide, *m*-chlorobenzotribromide and *p*-chlorobenzotribromide prepared by bromination procedures were analyzed with the following results. Calcd. for benzotribromide: Br, 72.90. Found: Br, 72.70. Calcd. for *m*-chlorobenzotribromide: mol. wt. 363.3; C, 23.14; halogen, 75.75. Found: mol. wt. (cryo.), 365; C, 23.00; halogen, 76.01. Calcd. for *p*-chlorobenzotribromide: mol. wt., 363; Cl, 9.76; Br, 65.98. Found: mol. wt. (cryo.), 365; Cl, 9.78; Br, 65.07.

The densities at 30.00 ± 0.01° of the pure liquids and benzene solutions were measured in 5-ml. and 100-ml. pycnometers, respectively. Results recorded in Table I are the average of not less than two separate measurements. Refractive indices of liquids were measured on an Abbe refractometer and of the solids on a Fisher refractometer equipped with a heater head. Freezing points were determined by the cooling curve method with a platinum resistance thermometer in an apparatus similar to that of Schwab and Wickers.[3] Melting points were determined for *o*- and *m*-chlorobenzotribromides by the heating curve method using a 0.1° thermometer and for *p*-chlorobenzotribromide and benzotribromide by use of a calibrated aluminum block.

The results of the solution density measurements are shown graphically as the solid lines in Fig. 1 where the ratio $\Delta d/f_2$ of the increment in density of the solution over that of pure benzene to the mole fraction of the solute is plotted against mole fraction of solute. The dotted lines are the ideal values of this ratio as a function of f_2 for the solutes that were liquid at 30°. The ideal value is derived from the relation

$$d_{12}^* = \frac{f_1 M_1 + f_2 M_2}{f_1 V_1 + f_2 V_2} \tag{1}$$

where V_1 and V_2 represent the respective molar volumes, f_1 and f_2 the mole fractions and d_{12}^* the ideal density of the solution assuming no change in volumes on mixing. After substitutions of $\Delta d^* = d_{12}^* - d_1$, $d_1 = M_1/V_1$, etc., and rearrangement, one obtains the relation

$$\frac{\Delta d^*}{f_2} = \frac{V_2}{V_1}\left[\frac{d_2 - d_1}{1 + f_2\left(\frac{V_2}{V_1} - 1\right)}\right] \tag{2}$$

The limiting values of $\Delta d/f_2$ and $\Delta d^*/f_2$ for each of the solutes are given in Table II along with the

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[2] A. L. Henne and M. S. Newman, This Journal, **60**, 1697 (1938).

[3] F. W. Schwab and F. Wickers, *J. Research Natl. Bur. Standards*, **34**, 333 (1946).

observed densities and the calculated density obtained by inserting the observed limiting values of $\Delta d/f_2$ and the appropriate values of V_1, V_2 and d_1 in equation 3 below.

$$\frac{\Delta d}{f_2}(\text{lim.}) = \left(\frac{V_2}{V_1}\right)(d_2 - d_1) \qquad (3)$$

TABLE II

Substance	d_2 (obsd.)	d_2 (lim.)	$\frac{\Delta d}{f_2}$ (lim.)	$\frac{\Delta d^*}{f_2}$	$\sum\frac{\Delta d}{f_2}$(lim)
Chlorobenzene	1.10	1.10	0.260	0.260	...
Dichlorobenzene	..	1.27	.519	(.519)	0.520
Benzotrifluoride	1.17	1.15	.398	.423	...
o-Chlorobenzotrifluoride	1.36	1.32	.686	.720	.658
m-Chlorobenzotrifluoride	1.33	1.29	.657	.695	.658
p-Chlorobenzotrifluoride	1.33	1.29	.658	.695	.658
Benzotrichloride	1.36	1.38	.802	.803	...
o-Chlorobenzotrichloride	1.51	1.52	1.10	1.08	1.06
m-Chlorobenzotrichloride	1.48	1.48	1.06	1.05	1.06
p-Chlorobenzotrichloride	1.47	1.48	1.06	1.05	1.06
Benzotribromide	..	2.22	2.23	(2.23)	..
o-Chlorobenzotribromide	2.26	2.34	2.54	2.48	2.49
m-Chlorobenzotribromide	2.21	2.28	2.50	2.45	2.49
p-Chlorobenzotribromide	..	1.27	2.50	(2.50)	2.49

The last column in Table II, $\Sigma\Delta d/f_2$(lim.), is obtained by adding the observed values of $\Delta d/f_2$(lim.) for the parent molecules: *viz.*, for *o*, *m*- and *p*-chlorobenzotrichloride the value of $\Delta d/f_2$(lim.) for chlorobenzene and benzotrichloride. The additivity of these values is quite good for the *meta* and *para* derivatives, and for the *ortho* cases is somewhat less satisfactory. In data for another series of measurements made on benzene solutions of the *o*-, *m*-, *p*-, fluoro-, chloro- and bromobenzotrifluorides in which the densities of the solutions were not so precisely determined as in the present work it was found that, including the *ortho* cases, the average deviation from additivity was approximately ±2.5%. In view of this it appears that the observed additivity of the limiting value of $\Delta d/f_2$ for a given solvent may be a rather general phenomena and thus may be useful in predicting densities of dilute solutions of derivatives if the appropriate values for the parent substances are known. A comparison of the observed and calculated values of the densities in Table II indicates that, in the series examined, approximate values of the density of the pure substances can be calculated by the method employed.

Examination of the graphs in Fig. 1 indicates that a reasonably good limiting value of $\Delta d/f_2$ can be obtained from a single measurement of a dilute solution if this is corrected assuming the slope of the $\Delta d/f_2$ *vs.* f_2 line is the same as for $\Delta d^*/f_2$ *vs.* f_2. If the value of $f_2((V_2/V_1) - 1)$ is small enough so that $1/[1 + f_2((V_2/V_1) - 1)]$ can be replaced by $1 - f_2((V_2/V_1) - 1)$ this slope is given by $(V_2/V_1)^2(d_2 - d_1)(V_2 - V_1)$.

The work of Kopp, LeBas and Traube on the additivity of atomic and molecular volumes has been reviewed by Smiles[4] and Kremann[5]; however, there appears to be no simple evident relation between the molar volume additivity and the additivity of $\Delta d/f_2$(lim.).

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[4] S. Smiles, "Relations Between Chemical Constitution and Some Physical Properties," Longmans, Green and Company, New York, N. Y., 1910, Chap. IV.

[5] R. Kremann, "Physikalischen Eigenschaften und Chemischer Konstitution," Theodor Steinkopff, Leipzig, Germany, 1937, Chap. III.

Radiochemical Purification of Nickel in Macro Quantities

BY S. E. SINGER[1] AND M. H. KURBATOV

RECEIVED APRIL 15, 1954

The authors were faced with the problem of purifying approximately 39 grams of neutron irradiated nickel to be used for the study of radiative electron capture in nickel-59.[2] Observation of the disintegration of this species is made difficult by the fact that the long half-life of 7×10^4 years together with the relatively low thermal neutron cross-section of 4.2 barns for nickel-58 restricts the amounts of activity obtainable to very small quantities. In addition, the phenomenon of radiative electron capture can be shown to amount to only 8×10^{-4} of the ordinary electron capture activity of nickel-59.[3] Thus in spite of the fact that the nickel sample was large and had been irradiated for 28 days with the highest thermal neutron flux then available (7×10^{12} neutrons/cm.^{2}/sec.), the total radiative electron capture activity was calculated to be only 1.2×10^{-7} curie. It was therefore necessary to undertake purification of the entire 39-g. sample in order to provide sufficient activity for study.

The classical procedure for the separation of nickel as the dimethylglyoxime complex is ordinarily restricted to amounts of nickel of the order of 10 to 30 mg. because of the low solubility of the reagent and the voluminous precipitate formed. Bickerdike and Willard[4] have shown that precipitation of this complex from homogeneous solution permits analysis of 100-mg. quantities of nickel. Similar results were obtained by Sweet and Harris.[5]

Experimental

A preliminary exploration of the possibilities of such a method for larger quantities of nickel was carried out as follows: A nitric acid solution containing approximately 4 g. of common nickel was diluted to one liter and the *p*H of the solution lowered to 0.8 with hydrochloric acid. The solution was placed in a five-liter round-bottom flask, 1200 ml. of a saturated solution of dimethylglyoxime in 95% ethanol were then added, followed by 200 g. of urea slurried in 200 ml. of water. The mixture was refluxed at the boiling point until samples of the supernate gave no test for nickel upon the addition of ammonium hydroxide. At *p*H 3.2, the supernate gave a positive test. The next check, at *p*H 5.9, gave a negative test for nickel. The latter *p*H was reached after approximately three hours of boiling. The resulting nickel complex was filtered through a medium porosity sintered glass funnel and washed with 50% ethanol to remove excess dimethylglyoxime. The precipitate consisted of minute, needle-like, brownish-red crystals, and was far less bulky than the usual nickel–dimethylglyoxime complex.

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[1] Headquarters, Air Force Special Weapons Center (ARDC), Kirtland Air Force Base, Albuquerque, New Mexico.

[2] W. S. Emmerich, S. E. Singer and J. D. Kurbatov, *Phys. Rev.*, **94**, 113 (1954).

[3] J. M. Jauch, Oak Ridge National Laboratory Report 1102 (1951).

[4] E. L. Bickerdike and H. H. Willard, *Anal. Chem.*, **24**, 1026 (1952).

[5] W. F. Harris and T. R. Sweet, unpublished data.