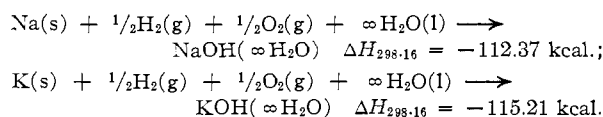pounds. Several years ago we published[1] data for the heats of reaction of sodium and potassium with water, from which the heats of formation of the hydroxide could readily have been calculated. Being interested in the other aspects of the data we did not make this simple calculation and furthermore 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.

(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

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

(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.

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.

(5) J. Traube, *Ber.*, **19**, 871 (1886), found the following viscosities: at 20°, 10% (wt. % *i*-PrOH in H$_2$O), 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]

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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

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