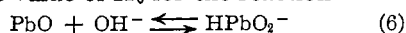


the only apparent solution to the uncertainty seems to lie in the constancy of the equilibrium constants determined over a wide range of concentration of alkali.

The data of Randall and Spencer are all higher than our values as well as those of Topleman. Randall and Spencer admit that their data for the yellow lead oxide show unaccounted-for irregularities.

It can be concluded that in the main the data of this research and those of Topleman are in agreement for the red form which is the stable form at room temperature; and even though there is no agreement in the data of these different researches for the yellow (olive) form, yet the constancy of the value of  $K_6$  for the reaction



seems to serve as an excellent criterion for the validity of the data of this research, which are extensive, are obtained from several preparations,

and are extended over a wide range of concentration of alkali.

### Summary

The solubilities of red, yellow, and black lead oxides and hydrated lead oxide were determined in water and in alkaline solutions.

From the data obtained the following calculations were made: (1) the degree of dissociation of lead hydroxide, (2) the  $\Delta F_{298}^\circ$  of formation of  $\text{HPbO}_2^-$ , (3) the  $\Delta F_{298}^\circ$  of ionization of  $\text{Pb}(\text{OH})_2$  as an acid and as a base, (4) the  $\Delta F_{298}^\circ$  difference between the two forms of lead oxide, and (5) the ionization constant for the second dissociation of  $\text{Pb}(\text{OH})_2$  as a base.

Evidence for the "formic acid" structure of the lead-bearing ion is submitted.

Some characteristics of black lead oxide are given.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WICHITA]

## Changes in Volume and Refractometer Readings Attending the Mixing of Cellosolve and Water and of Carbitol and Water at 25°C<sup>1</sup>

BY LLOYD MCKINLEY AND AGNES NIBARGER

The observation that pronounced contraction attends the mixing of water with cellosolve (ethylene glycol mono-ethyl ether, mol. wt. 90.09) or with carbitol (diethylene glycol mono-ethyl ether, mol. wt. 134.11) led to a determination of densities and refractive indices of solutions of these ethers<sup>2</sup> at concentrations through 0 to 100% of the organic component in 1% by weight intervals.

The solutions were made in a pair of 100-cc. volumetric flasks which in themselves proved to be satisfactory pycnometers when used in conjunction with a cathetometer. The capacity of such containers above the calibration marks permitted so many additions of water to initial 100-cc. portions of the organic liquid that most of the range was covered before the reverse procedure was employed with water as the sole contents. Following each addition, mixing and wait for the preparation to attain the temperature of the

water-bath, the withdrawal of excess solution provided a representative sample for the Abbe refractometer.

Since space is not available for the numerous tabulations arising from this study the results are in general depicted graphically only. Curves AB and AC of Fig. 1 indicate the reciprocal densities of aqueous solutions of cellosolve and of carbitol, respectively, whereas ab and ac show the corresponding refractometer readings.

The analytical rather than the graphical method for arriving at partial specific volumes by the intercept method was chosen. The equations found to fit AB are:

$$Y = 0.95169 + 0.001082 X - 0.055694 X^2; \quad (0 \text{ to } 18\% \text{ Cellosolve})$$

$$Y = 1.08155 - 0.002202 X - 0.041606 X^2 - 0.071233 X^3; \quad (18 \text{ to } 100\% \text{ Cellosolve})$$

where  $Y$  is the specific volume, and  $X$  is % by wt. water. Curve AC is satisfied by the equation,  $Y = 0.98938 + 0.02612 \sin(0.174 - 0.01 X)$ , where  $Y$  is the specific volume,  $X$  is % by wt. carbitol, and the angle is in pi radians.

(1) Original manuscript received April 14, 1938.

(2) These ethers were obtained from Carbide and Carbon Chemicals Corporation in a request which specified "high purity." The cellosolve was used as received. The carbitol, however, proved so hygroscopic that use was made only of that fraction which distilled at about 192° into a receiver with a tower of dehydrite.

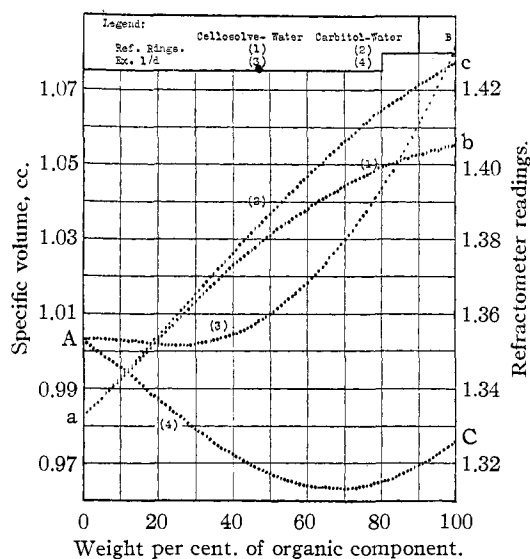


Fig. 1.—Specific volumes and refractometer readings of aqueous solutions of cellosolve and of carbitol.

The reliability of these equations for calculating specific volumes is expressed in Fig. 2. For both series, the points below the *O*-axis exceed those lying above it. Accordingly, calculated specific volumes if not in exact agreement with observed values will in general be too low. The

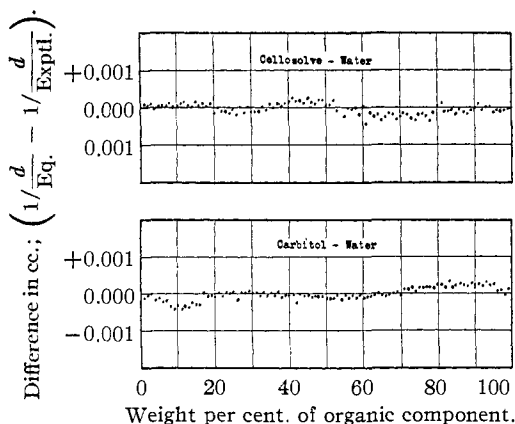


Fig. 2.—Departure of calculated specific volumes from reciprocal experimental densities.

mean deviation between the observed and calculated reciprocal densities is 0.00012 cc. for the cellosolve solutions, and 0.00014 cc. for the carbitol series. Despite some marked limitations these equations are offered as a more reliable device for evaluating intercepts by way of familiar analytical principles than that of mechanical extrapolation.

The concentration at which the partial molal volume (Fig. 3) of the organic component exhibits a minimum and that of water shows a maximum is about the same for both series and is not far, if any, removed from that designated for water-alcohol.<sup>3</sup>

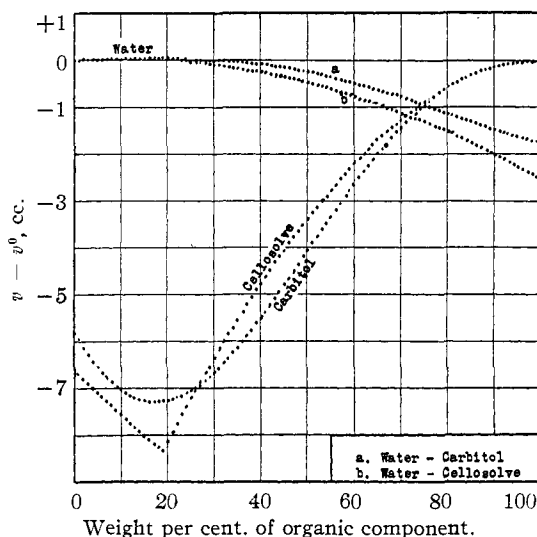


Fig. 3.—Partial molal volumes of carbitol, cellosolve and water.

Calculations applied to the equations for the specific volumes of Fig. 1 reveal that the minimum for AB is 24.98% cellosolve, whereas that for AC is at 67.40% carbitol. These quantities along with the corresponding calculated densities which are 0.99846 and 1.03814, respectively, are well in line with the direct observations of 0.99841 for 25.000% cellosolve and 1.03815 for 67.999% carbitol. These data, however, do not establish the concentrations at which preparations are attended by the most contraction.

The maximum departure of AB from a straight line joining A and B, the specific volumes of the pure components, is at 52% cellosolve for which solution the ideal specific volume is 1.04382 whereas the reciprocal of the observed density is 1.01129. In the preparation of 1000 cc. of such a solution there is a contraction of 32.53 cc. Similarly, it can be shown that the shrinkage attending the preparation of carbitol solutions is most pronounced at 57% carbitol and amounts to 22.79 cc. per 1000 cc.

Since the specific volume of pure cellosolve is 1.08155, and the partial specific of this component

(3) Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 40.

in a 52% solution is only 1.04726, it follows that cellosolve itself has a volume diminution of 17.29 cc. in a 1000 cc. preparation. For the carbitol solution just designated, the volume changes experienced by water and carbitol amount to 9.66 and 12.36 cc.

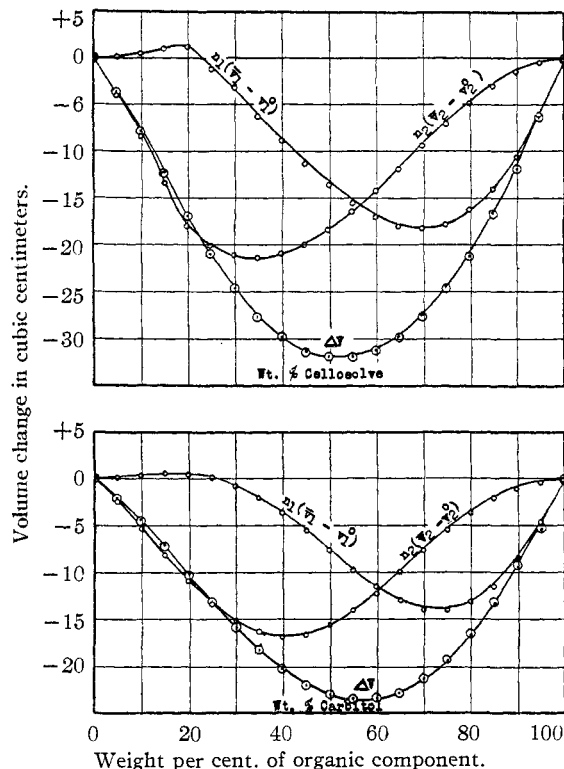


Fig. 4.—Changes in volume attending the preparation of 1000-cc. portions of aqueous solutions of cellosolve and of carbitol at 25°.  $1000(1/d - 1/d_i) = \Delta V = n_1(\bar{v}_1 - v_1^0) + n_2(\bar{v}_2 - v_2^0)$ .

The role of each component in the volume change attending the preparation of aqueous solutions of cellosolve and of carbitol for a series

of concentrations in 5% intervals is shown in Fig. 4.

The curves of Fig. 5 indicate that the maximum departure of refractometer readings from those termed ideal occurs approximately at the same concentration at which specific volumes depart most from the ideal or where the operation of mixing is attended by the most shrinkage.

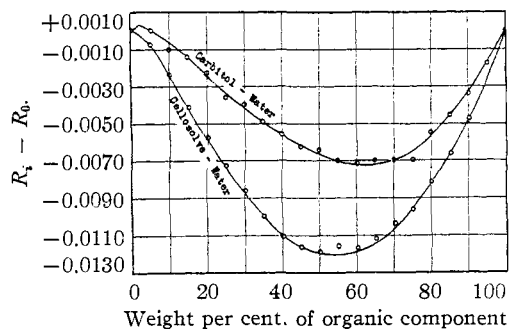


Fig. 5.—Departure of refractometer readings from those falling on a straight line connecting the indices of the pure components.

### Summary

Equations are offered which fit the specific volume curves of aqueous solutions of cellosolve and of carbitol at 25°. Accordingly, an analytical method for ascertaining partial specific volumes by the intercept method was realized.

The volume changes which attend the mixing of components are represented graphically for all concentrations. The region through which actual specific volumes depart most from the ideal does not include that concentration at which the observed specific volume is a minimum but does coincide with that range for which refractometer readings deviate most from a straight line connecting the indices of the pure components.