weight is taken as 196.07 g. No unusual behavior of the substance was observed; the heat capacity increases in a regular manner from 3.888 cal./deg. mole at 52.30°K. to 33.09 at 296.95°K.

The entropy increment between 51.00 and 298.16°K. was obtained by Simpson-rule integration of the C_p against log T plot as 29.18 cal./deg. mole. To obtain the entropy below 51.00°K., the measured heat capacity values were fitted with an empirical sum of Debye and Einstein functions, $D(200/T) + 3E(373/T) + 3E(760/T) + E(1551/T)$. This sum represents the data over the entire measured range to within 0.5% and gives 1.70 cal./deg. mole as the entropy at 51.00°K. The entropy at 298.16°K. is $S^0_{298.16} = 30.9 \pm 0.2$ cal./deg. mole.

The entropy of sphene at 298.16°K. and other entropy values compiled by Kelley[2] lead to $\Delta S_{298.16} = -0.6 \pm 0.3$ for the entropy of formation from calcium oxide, quartz and rutile. Likewise, the entropy of formation from wollastonite ($CaSiO_3$) and rutile is $\Delta S_{298.16} = -0.7 \pm 0.3$, and from perovskite ($CaTiO_3$) and quartz, $\Delta S_{298.16} = 0.0 \pm 0.3$.

The heat content measurements for the temperature range 298 to 1811°K. also were made with previously described apparatus.[1] The results, expressed in defined calories per mole, are in Table II and Fig. 1.

TABLE II

MEASURED HEAT CONTENT VALUES ABOVE 298.16°K.

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
375.4	2,735	1006.1	30,220	1579.6	59,170[a]
478.4	6,815	1105.4	35,050	1636.0	63,140[a]
579.2	10,980	1194.2	39,310	1665.4	74,740[a]
675.9	15,170	1296.5	44,240	1675.4	92,880
691.9	15,820	1387.8	48,740	1679.5	93,250
811.2	21,330	1495.5	54,110	1748.3	97,800
902.2	25,490	1542.3	56,770[a]	1811.7	102,030

[a] Values show premelting effects.

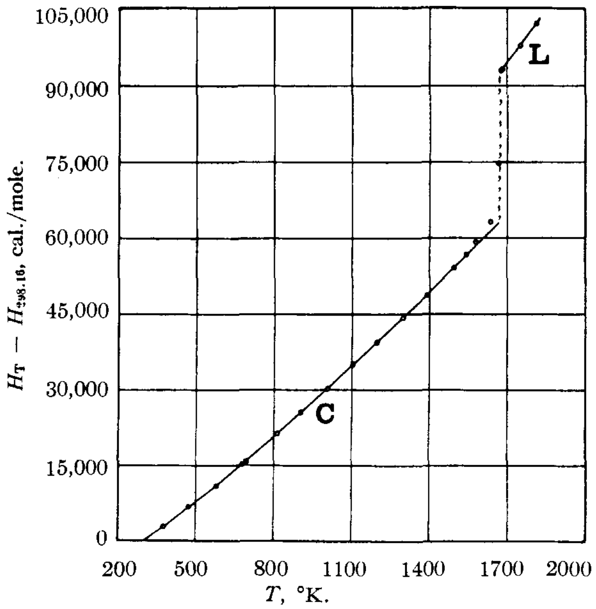

Fig. 1.—Heat content of $CaTiSiO_5$ above 298.16°K.: C, crystals; L, liquid.

The substance melts at 1,670°K., the heat and entropy of fusion being 29,590 cal./mole and 17.72 cal./deg. mole. The heat content of the crystals follows a regular course and averages about 2% less than the heat content sum for the constituent oxides. No evidence of premelting appeared below the 1,542.3°K.-point. This point and others labeled (a) in Table II show premelting effects. Assuming liquid-soluble, solid-insoluble impurities, the reported data indicate the purity of the sphene to be 99.0 mole %.

The heat content of the crystals between 298.16 and 1670°K. is represented by the following equation, with an average deviation of less than 0.3%

$$H_T - H_{298.16} = 42.39T + 2.77 \times 10^{-3}T^2 + 9.63 \times 10^5T^{-1} - 16{,}115$$

The heat content of the liquid increases linearly with temperature between 1670 and 1811°K. The measured results are represented to within 0.1% by the equation

$$H_T - H_{298.16} = 66.80T - 18{,}990$$

Table III contains smooth values of the heat content and entropy increments above 298.16°K. The latter were calculated to match the former by means of the method of Kelley.[3]

TABLE III

HEAT CONTENT AND ENTROPY INCREMENTS ABOVE 298.16°K.

T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg. mole	T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg. mole
400	3,750	10.78	1300	44,430	62.87
500	7,690	19.56	1400	49,350	66.51
600	11,860	27.16	1500	54,340	69.96
700	16,230	33.89	1600	59,400	73.22
800	20,750	39.93	1670	62,980(c)	75.41
900	25,380	45.38	1670	92,570(l)	93.13
1000	30,070	50.32	1700	94,570	94.32
1100	34,800	54.83	1800	101,250	98.14
1200	39,580	58.99			

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(2) K. K. Kelley, *U. S. Bur. Mines Bull.*, 477 (1950).

(3) K. K. Kelley, *ibid.*, 476 (1949).

Studies in Low Concentration Chemistry. IX. Some Investigations on Zinc

BY GEORGE K. SCHWEITZER AND WM. N. BISHOP

RECEIVED APRIL 30, 1954

The purpose of these studies was to investigate the radiocolloidal properties,[1] solvent extraction characteristics[2] and the tendency spontaneously to deposit on platinum foil[3] of zinc in low concentration aqueous solutions using zinc-65 as a radioactive tracer.

(1) G. K. Schweitzer and W. M. Jackson, *J. Chem. Educ.*, **29**, 513 (1953).

(2) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, p. 72; J. F. Steinbach and H. Freiser, *Anal. Chem.*, **25**, 881 (1953); C. B. Cook and J. F. Duncan, "Modern Radiochemical Practice," Oxford University Press, New York, N. Y., 1952, p. 11.

(3) G. K. Schweitzer and D. L. Wilhelm, THIS JOURNAL, **75**, 5432 (1953).

Experimental

Preparation of Zinc Solutions.—Zinc-65 was obtained as zinc chloride in hydrochloric acid solution from the Oak Ridge National Laboratory. The nuclide has a half-life of 250 days, and decays by electron capture, the emission of positrons and the emission of γ-rays.[4] The original solution was diluted to give the proper strength of radioactivity and the resulting solution was found to be about 10^{-6} *M* in zinc by use of the dithizone test.[5] Carrier solutions of zinc chloride of concentrations 10^{-4} and 10^{-2} *M* labeled with the radioactive zinc also were prepared. All other chemicals were of reagent grade quality and all solutions were prepared with distilled water.

Adjustment of *p*H.—The various solutions were adjusted to desired *p*H values by adding either sodium hydroxide or hydrochloric acid solution. Measurements of *p*H were made on a Beckman Model G-2 Glass Electrode *p*H Meter equipped with microelectrodes.

Sample Preparation.—Samples were taken with a 0.100-ml. micropipet and syringe. These samples were placed on copper or steel planchet or glass cups and evaporated to dryness under a heat lamp.

Radioactivity Apparatus.—Radioactivity measurements were made with a Nuclear D-33 end-window counting tube mounted in a Tracerlab SC-10 sample holder, attached to a Tracerlab SC-2A scaler. All samples were counted for a sufficiently long time to give standard deviations equal to or less than 1%.

Centrifugation.—Portions of the radioactive zinc solution originally 0.01 *M* in hydrochloric acid were adjusted to desired *p*H values, placed in centrifuge tubes holding 0.7 ml., sampled, centrifuged for 30 min. at about 25,000 times gravity in a Misco Microcentrifuge, and finally resampled. The differences in radioactivities were used as measures of the amounts of zinc removed.

Studies were carried out using 10^{-6}, 10^{-4} and 10^{-2} *M* zinc solutions. To correct for adsorption onto glass from the 10^{-6} *M* solutions, portions were adjusted to desired *p*H values, placed in centrifuge tubes, sampled, allowed to stand for 30 min., and then resampled. The amount adsorbed was subtracted from the amount removed during centrifugation to give the net amount centrifuged. Such corrections were found to be unnecessary for the 10^{-4} and 10^{-2} *M* solutions.

Extraction.—For investigating the extraction of zinc into acetylacetone from a water solution, it was desirable to have both phases remain at a constant volume during each experiment. Water at desired *p*H values and acetylacetone were allowed to stand in contact overnight, the mixture being stirred all the time. The layers were then separated and small amounts of radioactive zinc solution were added to the aqueous phase to give the proper concentration of zinc. Five-ml. portions of each phase were stirred together for 30 min., after which the layers were separated and samples taken from each. The radioactivities were employed to calculate the per cent. of zinc extracted into the acetylacetone. The extraction vessel was a 50-ml. distillation flask which had been cut off below the side-arm. The temperature was held at 25.0 ± 0.5° throughout the extraction by use of a Sargent constant temperature bath. These experiments were performed using 10^{-6}, 10^{-4} and 10^{-2} *M* zinc solutions originally 0.01 *M* in hydrochloric acid.

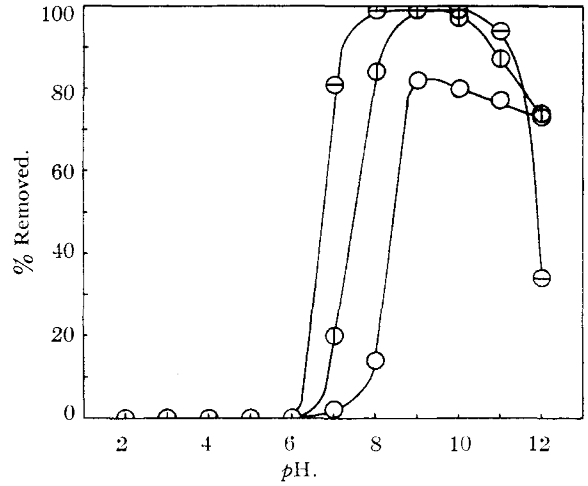

Fig. 1.—Per cent. zinc removed by centrifugation as a function of *p*H from solutions of zinc concentration 10^{-6} *M* (O), 10^{-4} *M* (⦶) and 10^{-2} *M* (⊖).

Spontaneous Depositions.—Solutions 10^{-6} *M* in zinc, originally 0.01 *M* in hydrochloric acid, were adjusted to various desired *p*H values. A strip of platinum foil 2 by 2 cm. was held upright in the solution which was stirred for 2 hours in a paraffin-lined 30-ml. beaker. Samples of the solution were taken periodically. Tests indicated that no corrections for adsorption onto the paraffin were necessary.

Results and Discussion

All of the following results are the averages of at least three separate determinations, none of the average values showing a standard deviation greater than 2.5 percentage points.

Centrifugations of solutions of the three different concentrations of zinc at various *p*H values show similar curves, as illustrated in Fig. 1. Calculation of the solubility product, setting the solubility product equal to the zinc concentration multiplied by the hydroxide concentration for 50% centrifugation squared, gives a value of about 10^{-17} in all three curves. This is in close agreement with the solubility product reported by Feitknecht and Haberli.[6] The trend for increased removal at a given *p*H value as the zinc concentration increases is the expected one, this trend being opposite to the one reported for several radiocolloidal elements.[7] This and the apparent agreement of the solubility product with the removal data lead to the belief that zinc is not exhibiting typical radiocolloidal behavior. The 10^{-2} *M* zinc solution showed a marked drop in the removal by centrifugation at high *p*H values. This probably is due to the formation of soluble zincate ions.[8]

The extraction studies as a function of *p*H values between 0.0 and 8.5 showed very little variation in per cent. extracted as the zinc concentration was altered and agree very well with the data of Steinbach and Freiser.[2] As the concentration of zinc increased a slight rise in the per cent. of zinc extracted was evidenced at *p*H values between 5.0 and 7.5. A self-salting action would seem to be a reasonable explanation for this behavior.[9]

The deposition studies indicated a maximum removal at and above a *p*H value of 9.0. From *p*H values of 1.0 to 5.0, no zinc was removed, and from a *p*H value of 5.0 to one of 9.0 the per cent. removed increased almost linearly from 0 to 18. Only 18% of the zinc could be removed from solution in 2 hours. The rate studies showed a gradual increase in removal for about 25 min., after which a plateau was observed, the rate curves at all *p*H values be-

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[4] J. M. Hollander, I. Perlman and G. T. Seaborg, *Rev. Modern Phys.*, **25**, 500 (1953).

[5] I. Mellan, "Organic Reagents in Inorganic Analysis," The Blakiston Company, Philadelphia, Pa., 1941, p. 616.

[6] W. Feitknecht and E. Haberli, *Helv. Chim. Acta*, **33**, 922 (1953).

[7] J. D. Kurbatov and M. H. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942); M. H. Kurbatov and J. D. Kurbatov, *J. Chem. Phys.*, **13**, 208 (1945); J. D. Kurbatov and A. M. Silverstein, *J. Phys. Colloid Chem.*, **54**, 1250 (1950); G. K. Schweitzer and W. N. Bishop, THIS JOURNAL, **75**, 6330 (1953).

[8] R. Scholder and H. Weber, *Z. anorg. Chem.*, **215**, 355 (1933).

[9] N. H. Nachtrieb and R. E. Fryxell, THIS JOURNAL, **70**, 3547, 3552 (1948).

ing very similar. The deposition could be explained by assuming adsorption of insoluble hydroxo forms of zinc onto the platinum foil.

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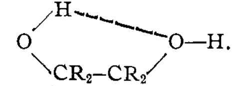
[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Hydrogen Bond. II. The Intramolecular Bond in Cyclic 1,2-Diols

BY LESTER P. KUHN

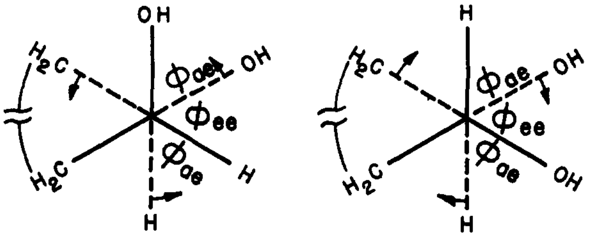
RECEIVED MARCH 5, 1954

The value of $\Delta\nu$, which is a measure of the length of the hydrogen bond, has been determined for a number of *cis* and *trans* cyclic 1,2-diols. The relationship between ring size and $\Delta\nu$ for both the *cis* and *trans* series is shown. In rings smaller than cyclodecane OH groups are closer together in the *cis* than in the *trans* diols. In rings larger than cyclodecane the OH groups of the *trans* isomer are closer together than those of the *cis*. Some conclusions are drawn concerning the constellation of cyclic compounds, and evidence is adduced which supports H. C. Brown's I-strain theory of the chemical reactivity of cyclic compounds.

In part I of this series,[1] it was shown that many dihydroxy compounds in dilute solution in carbon tetrachloride have two OH bands in the three-micron region. The higher frequency band is due to the free OH group and the lower frequency band is due to the bonded OH, indicating that these compounds exist in the form  $$\mathrm{O{-}H\cdots O{-}H,\ CR_2{-}CR_2}$$ The separation between the two bands, $\Delta\nu$, was found to increase as the length of the hydrogen bond decreases, thus in a series of closely related compounds where polarity differences are small, the observed values of $\Delta\nu$ can be used as a measure of the distance between the OH groups. In the work to be described here, this technique has been applied to a study of cyclic diols in which the H–O distance is determined by the constellation of the ring.[2]

The orientation of the exocyclic bonds around an endocyclic C–C bond is conveniently described by the angle ϕ which is defined as the angle formed by two exocyclic bonds as the observer looks down the axis of the C–C bond. This is illustrated for the cyclic 1,2-diols in Fig. 1 where the solid lines represent the bonds of carbon atom number 1 and the dashed lines represent the bonds of carbon number 2. The C–C bond is perpendicular to the plane of the paper. The angle that is formed by an axial and an equatorial bond[3] will be called ϕ_{ae}, and the angle formed by two equatorial bonds will be called ϕ_{ee}.

The positions of the OH bands of the *cis* and *trans* isomers of cyclic 1,2-diols containing 5, 6, 7, 8, 9, 10, 12 and 16 carbon atoms were carefully determined. The values of $\Delta\nu$ are shown in Table I.



cis. *trans.*

Fig. 1.

In using these data to draw conclusions concerning the constellation of the molecules studied, it is necessary to assume that (a) differences in $\Delta\nu$ between members of the series are due to differences in H–O distance, and (b) the bond angles and distances in the portion of each molecule containing the grouping –CHOH–CHOH– are the same. This means that the differences in H–O distance are due to differences in ϕ_{ae} for the *cis* diols and in ϕ_{ee} for the *trans* diols.

TABLE I

BAND SEPARATION OF CYCLIC 1,2-DIOLS

Compound, -1,2-diol	$\Delta\nu$ in cm.$^{-1}$	ϕ_{ae}, deg.	ϕ_{ce}, deg.
cis-Cyclopentane	61[a]	0	
trans-Cyclopentane	0[a]		<120
cis-Cyclohexane	38	50	
trans-Cyclohexane	33		60
cis-Cycloheptane	44	42	
trans-Cycloheptane	37		51
cis-Cyclooöctane	51	33	
trans-Cyclooöctane	43		44
cis-Cyclononane	49	36	
trans-Cyclononane	45		41
cis-Cyclodecane	44	42	
trans-Cyclodecane	45		41
cis-Cyclododecane	38	50	
trans-Cyclododecane	51		33
cis-Cyclohexadecane	..[b]	..	
trans-Cyclohexadecane	50		34

[a] Values taken from previous paper.[1] [b] Each band here was a doublet making it impossible to obtain an unambiguous value for $\Delta\nu$.

Using the methods of trigonometry, the relationship between ϕ and the H–O distance was calculated and is shown graphically in Fig. 2. It was as-

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[1] L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

[2] The term constellation is used to denote the geometric forms of cyclic compounds which arise by rotation around the C–C bonds, thus the chair and the boat forms of cyclohexane are possible constellations of this molecule: V. Prelog, *J. Chem. Soc.*, 423 (1950).

[3] It has been recommended that the two types of exocyclic bonds of cyclohexane, which have been previously called ϵ and K by some, and polar and equatorial by others, now be called axial and equatorial. This new nomenclature will be used here; D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Science*, **119**, 49 (1954).