

i.e., that the induced charges in I_2 are separated by $2r_1$ would give the second term in $U(r)$ as $-\epsilon^2\alpha/2r(r+r_1)^2$. The interaction energy, $U_2(r)$, calculated on this latter basis is given the suffix 2. The resultant energy of interaction will also include a term due to the work done in stretching the I_2 bond from its normal equilibrium value to that ($2r_1$) obtaining in the triiodide ion. Representing this (small) extension by x , the work done in stretching is $U_3(x) = 1/2! \times U^{II} \times x^2 + 1/3! \times U^{III} \times x^3 + 1/4! \times U^{IV} \times x^4 + \dots$, see ref. 22; the necessary values are tabulated by Herzberg.²³ Thus a theoretical ΔE_0 for $T = 0^\circ K.$ is given by $U(r_{eq.}) + U_3(x)$.

TABLE III

	$r_{eq.}$ Å. units	$2r_1$	$-U_1$ ($r_{eq.}$) erg per ion $\times 10^{13}$	$-U_2$ ($r_{eq.}$)	U_3 (x)	$-\Delta E_1$ cal. per g. ion	$-\Delta E_2$
a	3.23	2.68	2.00	2.30	0.00	2880	3310
b	3.15	2.76	2.08	2.43	0.61	2120	2630
c	3.09	2.82	2.13	2.51	1.55	840	1380
d	2.95	2.96	2.35	2.85	4.61	-3250	-2570

(22) See, W. Jevons, "Report on Band Spectra of Diatomic Molecules," The Physical Society, London, 1932, p. 27.

(23) G. Herzberg, "Molecular Spectra," Vol. I, Prentice-Hall Inc., New York, N. Y., 1939, p. 482, *et seq.*

Mooney's X-ray study²⁴ of the ammonium triiodide crystal structure provides the most direct estimates of $r_{eq.}$ and $2r_1$; these are given as 3.10 and 2.81 Å., as compared with the 2.67 Å. interatomic distance in the normal I_2 molecule. A number of values of ΔE_1 and ΔE_2 have been calculated, keeping $(r_{eq.} + 2r_1) = 5.91$ Å. These range from (a) where the I_2 molecule is unstretched during the interaction, to (d), which is a symmetrical I_3^- structure; (c) represents the distances proposed by Mooney.

The electrostatic calculation arrives at an energy close to the measured ΔH_T , but distinctly smaller than the present estimate, based on results between 298 and 336°K. only, of the more strictly comparable ΔH_0 . The pronounced temperature variation of ΔH_T has been taken to indicate that hydration effects play an important part during ion association in solution. This practical feature is one obvious item vitiating the agreement between calculated and experimental energy terms. Again, the simple treatment entirely neglects any contribution by electron sharing (*i.e.*, by exchange forces) which, clearly, may be a serious omission.

Acknowledgment.—One of us (E. G.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

(24) R. C. L. Mooney, *Z. Kristal.*, **90**, 143 (1935).

ABERYSTWYTH, WALES

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The System Cobaltous Chloride–Water–Acetone at 25°

BY LEONARD I. KATZIN AND JOHN R. FERRARO

RECEIVED OCTOBER 15, 1951

The phase diagram of the system cobaltous chloride–water–acetone at 25° is depicted. $CoCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 3H_2O$ are shown to exist over narrow ranges of water activity, in addition to the more generally accepted hydrates (hexahydrate, dihydrate, and probably monohydrate). The data do not determine the exact nature of the anhydrous cobalt chloride in the system, which could contain one or two molecules of acetone per cobalt chloride.

Cobaltous nitrate has been shown to form hydrates with six, four, three and two moles of water per mole of salt.¹ The literature on the hydrates of cobaltous chloride shows general agreement on the existence of hexahydrate and dihydrate, as well as a monohydrate. No trihydrate has been reported, and although descriptions of a tetrahydrate

and its preparation have been given,²⁻⁵ other workers have failed⁶⁻⁸ to find the tetrahydrate except⁹ as mixed crystals with manganous chloride. Cobaltous chloride tetrammine¹⁰ and tetrapyridine¹¹ are known, lending support to the thesis that a tetrahydrate exists. Since previous experience has shown the salt–water–acetone ternary system to be very favorable for detecting hydrates with narrow stability ranges,^{1,12} investigation was made of the cobaltous chloride–water–acetone system.

The results of the studies at 25° using the method of "wet residues" (Fig. 1 and Table I), taken together with the distinctive colors of those compositions, show the definite existence of $CoCl_2 \cdot 4H_2O$, and give evidence for the hitherto unreported trihydrate, $CoCl_2 \cdot 3H_2O$. Both have narrow stabil-

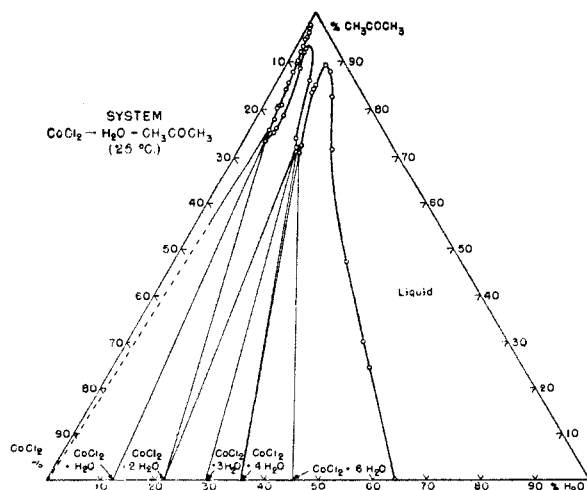


Fig. 1.

(1) L. I. Katzin and J. R. Ferraro, *THIS JOURNAL*, **72**, 5451 (1950).

(2) J. Bersch, *Sitzungsber. Akad. Wiss. Wien*, **56**(II), 724 (1867).

(3) W. O. de Coninck, *Bull. acad. roy. Belg.*, **803**, 1170 (1904).

(4) A. Neuhaus, *Chem. Erde*, **5**, 578 (1930).

(5) H. Benrath, *Z. anorg. allgem. Chem.*, **220**, 142 (1934).

(6) H. W. Foote, *THIS JOURNAL*, **45**, 663 (1923).

(7) A. Benrath, *Z. anorg. allgem. Chem.*, **163**, 396 (1927).

(8) H. Bassett and H. H. Croucher, *J. Chem. Soc.*, 1784 (1930).

(9) W. Stortenbeker, *Z. physik. Chem.*, **16**, 250 (1895).

(10) G. L. Clark, A. J. Quick and W. D. Harkins, *THIS JOURNAL*, **42**, 2483 (1920).

(11) Gmelin's "Handbuch der anorganischen Chemie," "Cobalt", (Sys. No. 58), 8th Ed., Verlag Chemie, Berlin, 1932, Abt. A, p. 294.

(12) L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).

TABLE I
 COBALTOUS CHLORIDE-WATER-ACETONE (25°)

Liquid % H ₂ O	Phase % CoCl ₂	Solid % H ₂ O	Phase % CoCl ₂	Equilibrium solid
64.52	35.72			
47.21	28.29	45.33	53.22	
43.23	26.83	45.48	53.39	
31.87	21.15	45.00	53.61	CoCl ₂ ·6H ₂ O
17.27	11.33	44.22	53.29	
11.61	5.79	43.98	53.56	
8.80	3.69	45.06	54.16	
7.25	3.60	44.09	53.92	
7.44	7.58	43.93	53.02	
7.47	8.42	45.33	53.62	
7.34	9.18	45.11	54.84	
10.89	16.73	44.53	53.59	
11.48	18.01	44.52	55.38	
11.12	17.61	42.85	55.62	CoCl ₂ ·6H ₂ O + CoCl ₂ ·4H ₂ O
11.32	17.97	37.28	57.67	
11.09	17.99	34.66	62.95	
11.12	18.28	34.12	65.46	
10.75	18.03	33.83	64.63	
10.74	18.25	32.31	66.08	CoCl ₂ ·4H ₂ O + CoCl ₂ ·3H ₂ O
10.70	18.19	32.16	62.69	
10.83	18.19	29.10	62.61	
10.06	17.49	26.95	62.34	CoCl ₂ ·3H ₂ O + CoCl ₂ ·2H ₂ O
10.34	17.58	26.80	61.30	
10.35	17.73	25.62	63.65	
9.18	16.95	19.63	65.73	
5.98	8.11	22.90	75.63	
1.71	5.67	19.38	65.23	CoCl ₂ ·2H ₂ O
1.71	6.25	19.28	64.20	
2.91	8.60	21.83	75.93	
4.74	16.57	21.49	73.32	
4.56	19.53	20.71	74.23	
4.66	20.11	18.84	66.51	
4.08	23.25	16.90	63.50	
3.95	22.95	12.67	67.87	CoCl ₂ ·2H ₂ O + CoCl ₂ ·H ₂ O
3.74	22.67	19.09	68.94	(?)
3.96	22.58	11.78	75.79	
3.53	23.09	10.83	66.75	
3.47	22.60	10.55	73.98	
3.36	20.94	10.97	72.15	CoCl ₂ ·H ₂ O (?)
3.48	18.68	7.93	57.18	
3.24	18.57	8.84	55.91	CoCl ₂ ·H ₂ O (?) + CoCl ₂ (?)
2.82	16.91	4.15	50.48	
2.68	16.69	3.95	38.16	
3.10	15.92	4.38	55.50	
2.15	13.49	3.93	37.84	
2.03	12.15	2.74	55.19	
1.72	10.15	2.21	47.99	CoCl ₂ (?)
1.76	8.54	3.43	52.16	
1.28	6.60	1.54	46.01	
1.06	5.70	1.73	48.33	
0.73	4.55	1.12	43.28	
0.95	4.08	2.77	44.40	
0.87	3.03	1.40	41.00	
0.43	2.52	1.24	32.85	
0.07	2.25	3.30	45.14	

ity ranges, judged by the small range of solution compositions with which they are in equilibrium, in contrast with the hexahydrate and the dihydrate. The color of the tetrahydrate is a distinctive

magenta, as has been described by others,^{4,5} very different from the red-brown of the hexahydrate, or violet of the dihydrate, or any mixture of these two colors. The color of the trihydrate tends toward a purple, which is also individual and not a blend.

It is also noticeable that the solubility of the cobalt chloride in the low-water end of the system is greater, on a mole fraction basis, than in the pure aqueous solution. This parallels the behavior already noted for the cobaltous nitrate¹ and uranyl nitrate¹² systems, and seems distinctly different from the situation with the chlorides of lithium, magnesium, calcium, barium, cadmium or cupric copper, with dioxane as the organic component.¹³⁻¹⁵ The failure to show the increased solubility in these last cases cannot therefore represent a general chloride-nitrate difference, and seems ascribable to a characteristic of the water activity coefficients in dioxane.¹⁶

The solubility curves of the hexahydrate and of the dihydrate are interesting, and apparently significant. With the first additions of the organic component, the solubility of the salt in the liquid phase drops, in the manner characteristic for many salts. When the cobalt concentration in the liquid phase has fallen to a value about 0.1 that of the pure aqueous solution, however, an upturn of the solubility commences, and finally the curve progresses essentially linearly in a direction extrapolating approximately to the composition CoCl₂·4H₂O. In the case of the dihydrate, from the fixed composition of the liquid in equilibrium with the trihydrate-dihydrate mixture, in the direction of lower water activity, the curve first progresses toward lower salt concentrations along a line, which, extrapolated toward the salt-water axis, passes approximately through CoCl₂·3H₂O. When the water-salt mole ratio in the liquid phase drops further, an upturn occurs in the solubility, with the linear portion of the curve extrapolating approximately to CoCl₂·2H₂O. With further decrease in the water activity in the system, the composition of the solid alters and the solubility of the salt drops off toward the value for the anhydrous condition. This behavior fits well with the relations deduced from spectrophotometric studies of cobaltous salts.^{16,17}

The initial drop on addition of acetone can be ascribed to removal of solvent water and increasing the activity coefficients of the ions, Co(H₂O)₆⁺⁺ and Cl⁻. As the water activity and concentration are lowered, the dielectric constant of the medium being lowered concomitantly, replacement of water with formation of [CoCl₂(H₂O)₄] begins to occur, and this neutral molecule may be expected to have a greater solubility in acetone than the ionized salt. As the concentration of cobalt chloride increases, in this region, the concentration of water should also increase, in the ratio four moles to one, giving the relation already noted in the experimental diagram.

(13) C. C. Lynch, *J. Phys. Chem.*, **46**, 366 (1942).

(14) H. F. Bogardus and C. C. Lynch, *ibid.*, **47**, 650 (1943).

(15) J. A. Weicksel and C. C. Lynch, *THIS JOURNAL*, **72**, 2632 (1950).

(16) L. I. Katzin and E. Gebert, *ibid.*, **72**, 5455 (1950).

(17) L. I. Katzin and E. Gebert, *ibid.*, **72**, 5464 (1950).

The solubility of the hexacoordinated form with three waters per salt molecule seems to be a maximum, similar to the case of cobaltous nitrate in *t*-butyl alcohol.¹ Therefore, the reduction of the water activity and concentration of the liquid phase, from the composition at which the solid changes from trihydrate to dihydrate, results in reduction of the concentration of cobalt chloride, in essence by eliminating $\text{CoCl}_2 \cdot 3\text{H}_2\text{O}$ from solution, to give the observed extrapolation. At some critical water activity, the equilibrium swings strongly to the side of the 4-coördinate condition, and $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ in the tetrahedral form¹⁷ apparently is more soluble than the trihydrated six-coördinate form, the cobalt chloride concentration increasing along a line extrapolating to $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ as the water activity is reduced.

The data seem to indicate that between the dihydrate and an anhydrous solid phase there occurs a solid with one molecule of water per molecule of salt. The data do not enable one to determine with certainty whether this is the normal monohydrate of cobaltous chloride, already known, or whether the solid might be a monohydrate-monoacetate. A similar uncertainty exists with the anhydrous solid—the data do not differentiate between unsolvated, monoacetate or diacetate material. An experimental impediment to resolution of the difficulty is the manner in which anhydrous CoCl_2 apparently imbibes acetone. Bell, Rowlands, Bamford, Thomas and Jones¹⁸ claim to have isolated $\text{CoCl}_2 \cdot \text{CH}_3\text{COCH}_3$, and report that it decomposes to

(18) W. R. G. Bell, C. B. Rowlands, I. J. Bamford, W. G. Thomas and W. J. Jones, *J. Chem. Soc.*, 1927 (1930).

CoCl_2 at 19.5°. If this report is correct, the anhydrous solid in our ternary system at 25° must be CoCl_2 , and the acetone retention of the solid must be due to the relatively powdery nature of the anhydrous material in contrast to the finely crystalline solids obtained at other positions in the phase diagram.

Experimental

General procedures and analytical methods have been described elsewhere.¹

Cobaltous Chloride.—The commercial chemically pure hexahydrate was used as stock material. The dihydrate was prepared from this by desiccation over concentrated sulfuric acid, under reduced pressure, for one week. The anhydrous salt was prepared by heating the dihydrate in an atmosphere of hydrogen chloride, and the composition was confirmed by analyses for cobalt and for water. A sample of monohydrate was prepared by long desiccation over concentrated sulfuric acid under reduced pressure.

Acetone.—The commercial pure liquid, free of substances reducing permanganate, was equilibrated with anhydrous potassium carbonate for 48 hours, and distilled with precautions to exclude water. The material so prepared gave final water analyses of 0.2–0.3% of water by weight, and treatment with calcium hydride, alumina, CuSO_4 , CaCl_2 or Na_2SO_4 gave no improvement. Although the pyridine-rich modification¹⁹ of the Karl Fischer reagent was used in the water analyses, it was possible that the residual quarter per cent. of water might be an analytical artefact, due to inadequate suppression of the ketone effect in the Karl Fischer titration. Our suspicion that a small water content of the order indicated might actually exist in well-dried acetone received some support from conductimetric experiments of others,^{20,21} but cannot be considered proven.

(19) D. M. Smith, W. M. D. Bryant and J. Mitchell, Jr., *THIS JOURNAL*, **61**, 2407 (1939).

(20) A. Lannung, *Z. physik. Chem.*, **A161**, 255, 269 (1932).

(21) K. J. Mysels, *J. Phys. Colloid Chem.*, **51**, 708 (1947).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WISCONSIN]

The Effect of Silica Gel Upon the Decomposition of Hydrogen Peroxide¹

BY S. S. PENNER²

RECEIVED NOVEMBER 9, 1951

A study of the thermal decomposition of hydrogen peroxide in basic silica gels, formed by the addition of sodium silicate to sulfuric acid, shows that the formation of the gel has no effect upon the stability of H_2O_2 at room temperature. The existence of reaction chains during the thermal decomposition in the gel is indicated by a wall effect and during photochemical decomposition by quantum yields which are appreciably greater than one. The kinetics of the decomposition of H_2O_2 in the presence of the chloride-chlorine couple is the same in silica sol and gel. The quantum yield for photochemical decomposition in the neighborhood of λ 3650 is of the same order of magnitude in silica gel and sol. On the basis of these experimental findings it is concluded that the apparent correlation observed by Fells and Firth (for sols containing HCl) and by the present author (for sols containing H_2SO_4) between the end of an induction period for the decomposition of H_2O_2 and the gelation of the sol is not determined by the physico-chemical changes associated with gelation.

I. Introduction

The best known examples of chemical reactions in gelatinous media are concerned with studies of the Liesegang phenomenon.³ The formation of

(1) The work described in this article was performed in 1942 at the suggestion of Professor Farrington Daniels. The study of a chain reaction in silica gel appeared to be of interest in connection with work on reaction kinetics in gelatinous propellants. Publication has been delayed because of the pressure of other work. The author takes pleasure in expressing his appreciation to Professor Daniels for helpful advice throughout the course of the work.

(2) California Institute of Technology, Pasadena, California.

(3) Wo. Ostwald, *Kolloid-Z., Zsigmondy Festschrift*, **36**, 380 (1925); J. Alexander, "Colloid Chemistry," Vol. I, The Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1926, pp. 783–807.

crystals in gels has been studied by Holmes.⁴ Fells and Firth⁵ used hydrogen peroxide to produce gas bubbles in silica gels and substantiated earlier findings by Hatschek⁶ who had described and studied the formation of lenticular gas bubbles in gels in contrast to the spherical bubbles observed in liquids. Fells and Firth reported that the change from spherical to lenticular bubbles occurred gradually as the sol set to a gel, an observation which is in agreement with every other physico-

(4) H. N. Holmes, *J. Phys. Chem.*, **21**, 709 (1916).

(5) H. A. Fells and J. B. Firth, *Proc. Roy. Soc. (London)*, **114A**, 517 (1927).

(6) E. Hatschek, *Kolloid-Z.*, **15**, 226 (1914).