The behavior of gases and liquids is represented by a p,v,T-surface, the variations of a saturated liquid and its vapor in equilibrium by a p,v,T-line.

TABLE V

$p(v_g + v_L + 2B)/CT$ (FOR EXPERIMENTAL p, v, T-VALUES)

Water,[5] $C = 0.0045548$, $B = 0.0035593$

T, °C.		T, °C.		T, °C.	
0	0.9994	140	0.9794	280	0.9702
20	.9980	160	.9744	300	.9792
40	.9971	180	.9687	320	.9916
60	.9956	200	.9649	340	1.0074
80	.9930	220	.9621	350	1.0157
100	.9892	240	.9618	360	1.0203
120	.9846	260	.9641	374.11	(1.0000)

Dichlorodifluoromethane,[6] $C = 0.00067861$, $B = 0.0014974$

−40.00	0.9933	10.00	0.9945	60.00	1.0003
−23.33	.9920	26.67	1.0006	111.5	(1.0000)
− 6.67	.9912	43.33	1.0025		

Propyl acetate,[2] $C = 0.00080349$, $B = 0.0033244$

101.55	0.9766	180	0.9795	260	1.0360
120	.9788	200	0.9859	275	1.0221
140	.9730	220	0.9996	276.2	(1.0000)
160	.9763	240	1.0160		

This line of saturation is part of the p,v,T-surface, therefore, a direct comparison of the equations here presented and other equations of state is possible.

Summary

1. A relationship between the volumes, the pressure and the temperature of saturated fluids is derived which also affords a mathematical expression of the line of saturation.

2. Mathematical expressions for the sum and for the difference of the volumes of saturated liquids and vapors are deduced.

3. The relationship was tested on 58 substances and found to be more accurate in this region than 3-constant equations such as van der Waals' or Berthelot's.

COMMONWEALTH COLOR AND CHEMICAL CO.
BROOKLYN, N. Y.
RECEIVED NOVEMBER 27, 1945

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[5] Fales and Shapiro, THIS JOURNAL, **58**, 2418 (1936); Osborn and Meyers, *Bur. Standards J. Research*, **13**, 1 (1934); Smith, Keyes and Gerry, *Proc. Am. Acad. Arts Sci.*, **69**, 137, 139 (1934).

[6] Perry's "Chem. Eng. Handbook," 2nd ed., p. 2574 (1941).

[CONTRIBUTION FROM THE NCHANGA CONSOLIDATED COPPER MINES LIMITED, CHINGOLA, NORTHERN RHODESIA]

The Entrainment of Cobalt and Sulfur in Iron Separations

BY E. T. PINKNEY, R. DICK AND R. S. YOUNG

Introduction.—It has long been observed by analytical chemists that cobalt is very tenaciously held in a ferric hydroxide precipitate formed by adding ammonia to a solution containing iron and cobalt. The difficulty of separating cobalt from iron with ammonia has been recognized by the use of the zinc oxide or ether separations in cobalt analyses for many years, and latterly by the employment of a phosphate to remove iron. Iron may of course also be separated from cobalt by the aid of cupferron or by pyridine.[1,2] Iron and cobalt may be removed in a sulfur determination by electrolysis with a mercury cathode.

In the metallurgical industries, iron is sometimes removed with ammonia prior to the precipitation of barium sulfate in a sulfur determination. It was noticed in this laboratory, working with samples of cobalt and iron sulfates, that one or two precipitations with ammonia gave complete recovery of sulfur, whereas cobalt was still heavily entrained in the ferric hydroxide precipitate. An investigation of the entrainment of cobalt and sulfur in iron separations appeared desirable.

Experimental Procedure and Results

A standard solution was made up from B.D.H. AnalaR cobalt sulfate and Merck analyzed ferric sulfate to contain approximately the quantities commonly found in many local metallurgical samples. The values were checked by careful analyses and found to represent the following in grams per liter: Co 3.92, S 5.72, and Fe 3.88.

In the first experiments 25-ml. aliquots, representing 0.0980 g. Co, 0.1430 g. S, and 0.0970 g. Fe, were treated in the standard manner for the separation of iron using trisodium phosphate, ammonium hydroxide and ammonium chloride, and zinc oxide, respectively. One precipitation only was made, the sample was filtered immediately after boiling, and the quantity of hot wash water was kept constant throughout. Cobalt and sulfur were determined on different aliquots in each case after separation of the iron. The results shown in Table I are typical of those obtained.

TABLE I

RETENTION OF COBALT AND SULFUR IN IRON PRECIPITATES

	% Recovery in first filtrate			
	First series		Second series	
Precipitant for iron	Co	S	Co	S
Na_3PO_4	99.6	99.8	99.5	99.3
NH_4OH and NH_4Cl	73.7	99.6	67.2	99.4
	87.0	99.3		
NH_4OH and $(NH_4)_2CO_3$	..	..	53.9	98.9
ZnO	98.3	95.8	95.8	95.0

In the second series cobalt and sulfur were

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[1] Spacu, *Compt. rend.*, **200**, 1595 (1935).

[2] Lingane and Kerlinger, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 77 (1941).

determined on the same aliquot, after the iron separation, by precipitating sulfur as $BaSO_4$ and recovering cobalt from the $BaSO_4$ filtrate by precipitating with α-nitroso-β-naphthol, igniting to oxide, taking into solution, and electrolyzing the cobalt. Since the first experiments showed that the retention of cobalt and sulfur in a phosphate separation was extremely small, the iron hydroxide precipitates were dissolved in hydrochloric acid, iron separated with phosphate, and cobalt and sulfur determined on this filtrate. Small quantities of cobalt were determined by means of nitroso-R-salt, using a Spekker photoelectric absorptiometer. By this means an overall check on the quantities of cobalt and sulfur present was obtained, and in all cases the sum of the constituents found in precipitate and filtrate equalled the amount originally added, within the usual limits of experimental error. Careful blanks were run throughout. The solutions were again filtered hot and washed with a measured quantity of hot water.

The results indicate clearly that the phosphate separation of iron gives a practically complete recovery of both cobalt and sulfur in one precipitation. This, of course, has been recorded for cobalt,[3] but to our knowledge this fact has not been previously noted for sulfur. Zinc oxide separation of iron, when filtration is carried out in hot solution, does not give a satisfactory recovery of either cobalt or sulfur with one precipitation. It is well recognized that for exact cobalt analyses a second, or in some cases even a third, precipitation of iron with zinc oxide is necessary, and apparently sulfur is retained to approximately the same extent under these conditions. Ferric hydroxide formed from ammonium hydroxide and ammonium chloride or ammonium carbonate shows practically no retentive power toward the sulfate ion, yet it entrains large quantities of cobalt, in some cases nearly 50% in the first precipitate. Another characteristic feature of the entrainment of cobalt by ammonium hydroxide separation of iron is the wide variation when conditions of ammonia concentration, temperature, washing, etc., are maintained as constant as possible in careful analytical work.

For routine cobalt determinations it is sometimes recommended to precipitate the iron with zinc oxide in a volumetric flask, make up to the mark, allow to settle, and decant an aliquot through a filter paper for the analysis.[4] When this was done it was found that although the cobalt in our samples was recovered in the first filtrate to the extent of 94–99%, a very low recovery of sulfur was obtained. This pointed to a marked influence of such factors as precipitating temperature, filtration temperature, etc., in the entrainment of sulfur in a zinc oxide separation of iron.

A number of analyses was carried out, varying the conditions of the zinc oxide separation, and the results are given in Table II. The same analytical procedures were employed as in the second series of Table I. It will be seen that the smaller the size of the sample the greater the recovery of sulfur and cobalt, especially the former. Precipitation in the cold leads to a lower retention of sulfur and a slightly lower entrainment of cobalt. Filtration of hot solutions gives a greater recovery, particularly of sulfur. The best results are secured by filtering hot, and in this case precipitation can be made in hot solutions with no ill effects. Filtering cold, regardless of whether precipitation was carried out in hot or cold solution, invariably gives low and erratic results for sulfur and slightly lower recoveries of cobalt. Precipitating hot and filtering cold gave the lowest recoveries of both cobalt and sulfur. Since the precipitate formed with ammonia from solutions of cobaltous salts is soluble in ammonium chloride,[5] the latter reagent was added in the zinc oxide separation in some cases with the hope that it might decrease occlusion of cobalt. The presence of ammonium chloride, however, was found to give a slightly lower recovery of cobalt and a significantly lower recovery of sulfur in the filtrate.

TABLE II

EFFECT OF VARIABLES ON RETENTION OF COBALT AND SULFUR IN ZINC OXIDE SEPARATION OF IRON

Size of aliquot, ml.	Precipitated	Filtered	Addition of NH_4Cl	Na_2CO_3 to neutralize excess acid	% Recovery in first filtrate Co	S
10	Hot	Cold	No	No	98	80
10	Hot	Hot	No	No	98	95
25	Hot	Cold	Yes	No	89	27
10	Hot	Cold	Yes	No	94	76
10	Hot	Cold	Yes	No	97	70
10	Cold	Cold	Yes	No	98	82
25	Hot	Cold	Yes	No	90	45
25	Cold	Cold	Yes	No	95	56
25	Hot	Cold	No	No	96	58
25	Hot	Hot	No	No	98	96
25	Hot	Hot	Yes	No	96	86
25	Hot	Cold	No	Yes	83	44
25	Cold	Cold	No	Yes	94	87
25	Hot	Hot	No	Yes	97	95

In some samples sodium carbonate was used to neutralize most of the acid prior to addition of zinc oxide, with the idea of decreasing the quantity of the latter present in the solution. This, however, merely resulted in a decrease of recovery of both cobalt and sulfur, and it does not appear that large quantities of zinc oxide increase the entrainment of cobalt and sulfur in this iron separation.

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(3) North and Wells, *Ind. Eng. Chem., Anal. Ed.*, **14**, 859–860 (1942).

(4) "Sampling and Analysis of Carbon and Alloy Steels," Reinhold Publ. Corp., New York, N. Y., 1938, p. 230.

(5) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XIV, Longmans, Green & Co., London, 1935, p. 515.

Summary

Cobalt and sulfur are entrained to various degrees when iron is separated by means of phosphate, ammonia and ammonium salts, and zinc oxide. A single phosphate separation leaves practically no cobalt or sulfur in the precipitate. Separation of iron with ammonia and ammonium salts gives almost complete recovery of sulfur in one precipitation, but cobalt is very strongly entrained and a large number of re-precipitations are necessary to liberate this element completely from ferric hydroxide in ammoniacal solution. Separation of iron with zinc oxide if the filtration is performed hot yields most of the cobalt and sulfur in one precipitation, though the recovery is not satisfactory and for exact analyses a second precipitation is necessary. If filtration is done in the cold the retention of cobalt is slightly increased and the entrainment of sulfur is very markedly increased.

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NOTES

The Reaction between Triethylsilane and Methyllithium

BY HENRY GILMAN AND SAMUEL P. MASSIE, JR.

In connection with studies concerned with the preparation of lithium triethylsilicide, $(C_2H_5)_3SiLi$, an examination was made of the reaction of triethylsilane with methyllithium. The course of reaction is apparently best expressed as

$$(C_2H_5)_3SiH + CH_3Li \longrightarrow (C_2H_5)_3Si(CH_3) + LiH$$

An examination is being made of some other related hydrides, particularly those of germanium and tin.

Kraus and Nelson[1] in a comprehensive study of reactions in liquid ammonia and in liquid ethylamine presented convincing evidence for the preparation of lithium triethylsilicide by an indirect procedure. They showed that triphenylgermanyltriethylsilane was cleaved by lithium in liquid ethylamine to give lithium triphenylgermanide and lithium triethylsilicide.

$$(C_6H_5)_3Ge\text{-}Si(C_2H_5)_3 + 2Li \longrightarrow (C_6H_5)_3GeLi + (C_2H_5)_3SiLi$$

The salts could not be separated and identified as such, but their formation was demonstrated by reaction of the mixture of salts with ammonium bromide to give triphenylgermane and triethylsilane; and by reaction with ethyl bromide to give ethyltriphenylgermanium and tetraethylsilicon.

Experimental

First, silicochloroform was prepared[1] from dry, finely powdered ferrosilicon[2] by heating in a stream of hydrogen chloride for ten and one-half hours at 270–295°. Then, in accordance with the procedure of Kraus and Nelson,[1] the triethylsilane was formed by interaction of silicochloroform and ethylmagnesium bromide.

In a flask provided with a mercury-sealed stirrer, a dropping funnel, a condenser, and an outlet tube connecting with a Dry Ice trap and a gas-collecting bulb, was placed 0.064 mole of methyllithium[3] in 80 cc. of ether subsequent to sweeping out with dry nitrogen. On the slow addition, with stirring, of 7.7 g. (0.066 mole) of triethylsilane there was only a slight reflux. As the reaction proceeded the mixture increased in cloudiness, and after three and one-half hours Color Test I[4] was positive. However, the color test was negative after stirring an additional ten hours at room temperature and then refluxing for twelve and one-half hours. No gas was evolved. When stirring was stopped, a white solid settled out leaving a yellow supernatant liquid. The weight of solid obtained after filtration under nitrogen was 0.7 g. Analysis of the solid by treating an aliquot with water and measuring the hydrogen evolved, and then by titrating the aqueous hydrolysate with standard acid showed the solid to be composed of lithium hydride and a basic material which was largely lithium hydroxide. In a typical analysis 0.0108 g. of the solid gave on hydrolysis 9.63 cc. of hydrogen which corresponds to a 42% yield of lithium hydride. The total amount of lithium hydroxide as determined by titration of the hydrolysate was 0.000779 mole. The calculated quantity of lithium hydroxide on the basis of a 42% yield of lithium hydride, with the remainder of the solid being lithium hydroxide, is 0.000737 mole.

From the ether filtrate was obtained by distillation, 4.5 g. (54%) of triethylmethylsilicon; b. p., 119–123°; d^{20}_{20} 0.7420.

Anal.[5] Calcd. for $C_7H_{18}Si$: Si, 21.54. Found: Si, 21:56 and 21.66.

The yields of triethylmethylsilicon from two other reactions starting with 0.066 mole of triethylsilane were 3.0 g. (35%) and 3.3 g. (38%), respectively.

Triphenylsilane reacts with RLi compounds in the manner described for triethylsilane and methyllithium. However, under corresponding conditions there appears to be no reaction wih some Grignard reagents (studies by Horace Melvin).

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(1) Kraus and Nelson, THIS JOURNAL, **56**, 200 (1934).

(2) Furnished in part by Keokuk-Electro Metals Co., Keokuk, Iowa.

(3) Gilman, Zoellner and Selby, THIS JOURNAL, **55**, 1252 (1933). See, also, Gilman, Zoellner, Selby and Boatner, *Rec. trav. chim.*, **54**, 584 (1935).

(4) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

(5) The analysis for silicon was by the Parr bomb fusion procedure. See, Gilliam, Liebhafsky and Winslow, THIS JOURNAL, **63**, 802 (1941); Schumb, Ackermann, and Saffer, *ibid.*, **60**, 2488 (1938); and Tseng and Chao, *Science Repts. Natl. Univ. Peking*, **1**, (No. 4) 21 (1936) [*C. A.*, **31**, 655 (1937)].