I wish to express my thanks to Dr. H. E. Merwin of the Geophysical Laboratory for his invaluable help in the interpretation of these results and in their presentation.

Summary

The series of solid solutions that includes the minerals troilite and pyrrhotite extends from the compound FeS to approximately the composition $FeS_{1.14}$ at 300°. Thermal analyses of synthetic materials indicate that these solid solutions appear in six different forms between room temperature and 575°. However, thermal data alone are inadequate to preclude the possibility that one or more of these "forms" may in reality be a mixture of two distinct solid phases in equilibrium. A prompt, reversible transformation takes place in all of these compositions between 315 and 318° and there is strong evidence that the form *b*, stable just above 318°, is not the form *a* which is synthesized at 550–575°. In the compound FeS the form *c*, stable just below 315°, transforms reversibly between 144 and 139° to a new form *d* which appears to be the stable form of all these solid solutions at room temperature. With increasing sulfur content the temperature of this transformation is lowered and it becomes very sluggish. From FeS to about the composition $FeS_{1.05}$ the transformation is between forms *d* and *c*; at the latter point an intermediate form *e* appears and beyond about $FeS_{1.07}$ the transformation is between form *d* and an additional intermediate form *f*. Temperatures of transformations $c \rightleftharpoons e$ and $e \rightleftharpoons f$ are raised by increasing sulfur content, reaching the limit of solid solution very close together a few degrees below the $b \rightleftharpoons c$ transformation.

Washington, D. C. Received April 17, 1935

[Contribution from the Department of Chemistry, Greensboro College]

Ternary Systems: Water, Allyl Alcohol and Salts at 25°

By P. M. Ginnings and Mary Dees

Previous investigations[1-4] have revealed some interesting relationships in this class of systems. Consider the systems of the saturated, water soluble, aliphatic alcohols with various inorganic salts and water. It is not surprising to find that methanol is by far the most difficult to salt out, followed by ethanol and then by *n*-propanol. Also, rearrangement of the straight chain to the branched types which are present in the iso, secondary and tertiary compounds results in alcohols more difficult to salt out. This is entirely in accord with the theory, particularly if the solubilities of the four butanols in water are considered. If an arbitrary salting out scale is arranged with all of these alcohols placed thereon, the differentials between methanol and ethanol and between ethanol and *n*-propanol are large enough to more than nullify any preferential characteristics of the inorganic salt used. Any salt that will salt out (produce two liquid phases) with methanol will invariably do the same to ethanol. Similarly, *n*-propanol will always be salted out by any salt that salts out ethanol. However, three of these saturated alcohols—isopropanol, *n*-propanol and *t*-butanol—are so similar in their solubility behavior that the preferential action of some salts in a few cases becomes sufficiently dominant that the usual order of these three alcohols on the salting out scale is changed. The reason for this unexpected change is not evident at present. However, with a few exceptions isopropanol is more difficult to salt out than *n*-propanol and the latter slightly more so than *t*-butanol.

The main object in the present work was to study the effect of the change from a saturated to an unsaturated group in the alcohol molecule upon the salting out characteristics and to compare this with the effect that occurs when the straight molecular chain is rearranged to a branched configuration. The mathematical aspects were also investigated in connection with the quantitative data. Search of the literature revealed only one pertinent paper on this particular subject[5] in which data on the systems of allyl alcohol with four salts were reported. Since reliable comparisons with such limited data are difficult, qualitative tests with allyl alcohol,

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(1) Ginnings and Robbins, This Journal, **52**, 2282–2286 (1930).
(2) Ginnings and Chen, *ibid.*, **53**, 3765–3769 (1931).
(3) Ginnings, Herring and Webb, *ibid.*, **55**, 875–878 (1933).
(4) Ginnings, Webb and Hinohara, *ibid.*, **55**, 4898–4899 (1933).
(5) Frankforter and Temple, *ibid.*, **37**, 2709–2715 (1915).

water and many common inorganic salts were tried. A study of the results compared with the data available for isopropanol and *n*-propanol revealed that allyl alcohol is salted out by fewer salts than either isopropanol or *n*-propanol. Furthermore, it has been found in connection with some other work now in progress that the critical solution temperatures of allyl alcohol systems (temperature below which a homogeneous solution of the three components will not form the two liquid phases) are always higher than those of isopropanol or *n*-propanol. Evidently, transition from the saturated to the unsaturated group in the molecule in this case has a greater effect than the rearrangement of the structure to isopropanol.

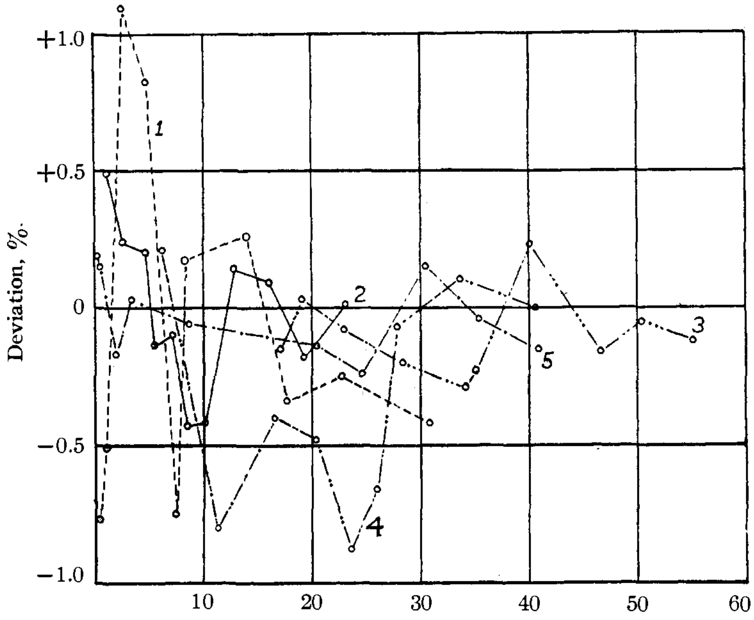

Fig. 1.—Deviation chart of experimental values of weight percentages of allyl alcohol from values calculated using the empirical equations.

Ten salts have been investigated quantitatively for the binodal curves and plait points. One of these (with sodium chloride) was determined at both 20 and 25° as an experimental check with Frankforter and Temple.[5] The results in this system were in good agreement throughout except it was found that the binodal curve extended further into the salt rich region. Empirical equations have been derived that fit the experimental data the best and the constants are given in Table I. Without exception, the exponential type of function fits the best of any tried and, as can be seen from the deviation curves, represents the experimental results with fair accuracy.

If details in regard to the methods and experimental procedure are desired, reference should be made to a previous paper[3] as the methods used here were almost identical. C. P. allyl alcohol of

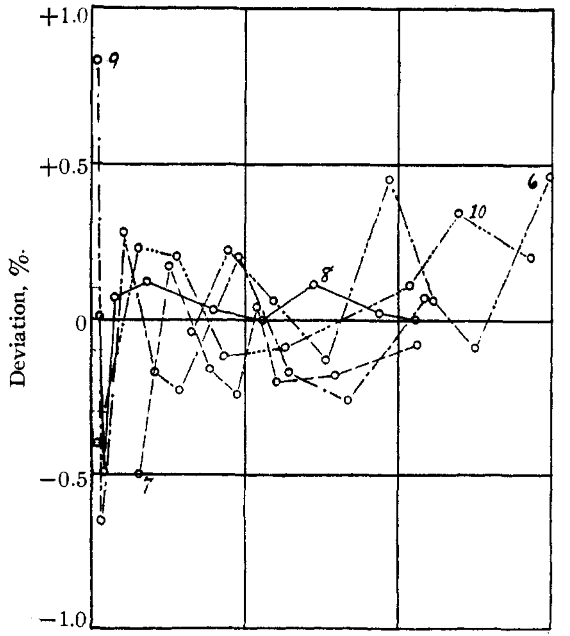

Fig. 2.—Deviation chart of experimental values of weight percentages of allyl alcohol from values calculated using the empirical equations.

d^{20}_{20} 0.8521 was used throughout this investigation, without purification. The authors feel that the results are not in error more than one per cent. in any case and that the accuracy usually exceeds this.

The tabular data given herewith are for use with the empirical equation $y = a + b\ (10)^{-cx}$, where y = weight percentage of allyl alcohol, x = weight percentage of salt and a, b and c are arbitrary constants.

TABLE I

Dev. curve	Salt	Alcohol rich section *a*	*b*	*c*	Limit for "x"	Salt rich section *a*	*b*	*c*	"x" at plait point
1	$(NH_4)_2HPO_4$	31.99	43.01	0.1837	6.0	0	56.0	0.03225	11.37
9	$Na_2S_2O_3$	35.60	41.67	.1696	5.0	0	66.6	.04025	7.93
8	$MgSO_4$	29.46	32.10	.2460	4.3	− 2.31	52.1	.04107	7.12
4	$NaNO_3$	−70.0	159.0	.00910	26.1	2.90	352.2	.04895	18.96
5	K_2CO_3	32.78	43.96	.1608	4.4	0.44	72.44	.0548	6.24
7	NaCl	17.6	84.50	.0625	8.6	0	128.8	.0565	8.90
6	$SrCl_2$	34.65	102.3	.07116	13.3	0	167.3	.04205	14.87
3	NH_4NO_3	0	112.1	.01402	32.5	0	198.0	.02165	33.45
10	$(NH_4)_2SO_4$	31.30	47.20	.1309	7.0	1.73	74.64	.04677	7.62
2	$CdSO_4$	31.27	30.90	.1545	4.9	−10.0	57.35	.01901	12.55

Summary

Data are given for the ternary systems of water and allyl alcohol with ten salts at 25°. From the qualitative and quantitative data, allyl alcohol seems to be more difficult to salt out than either isopropanol or *n*-propanol. The exponential function seems to express the relationship between the experimental data the best of any tried. Values for the numerical constants in the empirical equations and deviation charts are given for all of the systems.

GREENSBORO, NORTH CAROLINA
RECEIVED APRIL 22, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Recombination of Hydrogen Atoms in the Presence of Hydrogen Chloride

BY W. H. RODEBUSH AND M. L. SPEALMAN*

Rodebush and Klingelhoefer[1] measured the rate of the reaction

$$Cl + H_2 = HCl + H \qquad (I)$$

at several temperatures. The rate of the reverse reaction

$$H + HCl = Cl + H_2 \qquad (II)$$

may be calculated from their work, but since it is measurably slow it seemed desirable to measure it in order to reduce the uncertainty in the data for this reaction, especially as regards the temperature coefficient. A number of experimental difficulties were encountered which need not be detailed here. The equilibrium constant for (II) above may be calculated to lie between the values 1.6 and 8.5. The measurement is therefore made more difficult by the danger of approaching equilibrium. This difficulty was not encountered, however. What was actually observed was that the amount of chlorine obtained was a great deal less than the limiting equilibrium amount. At the same time, it was observed that a great deal of heat was liberated at the point in the apparatus where the hydrogen atoms came into contact with the hydrogen chloride, and the number of hydrogen atoms recombining was many times the number of hydrogen chloride molecules, so that the recombination would not be explained by any single simple mechanism. The recombination and heat evolution ceased on stopping the flow of hydrogen chloride. The problem, therefore, became one of determining in what way the hydrogen chloride brought about the recombination of the hydrogen atoms.

Experimental

In order to obtain a minimum of catalytic activity for the recombination of hydrogen atoms, the glass to be used was cleaned with hot chromic–sulfuric acid cleaning solution, rinsed with distilled water, then with acetone, and finally dried in a current of air. After *all* glassblowing operations (except, of course, connecting to the pumps and the leaks) were completed, the cleaning, rinsing and drying operations were repeated.

Hydrogen atoms were produced by means of the electrodeless discharge. It was found that a high degree of

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(*) This work was submitted by M. L. Spealman in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

[1] THIS JOURNAL, **55**, 130 (1933).