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A STUDY OF THE FACTORS INFLUENCING COMPOUND FORMATION AND SOLUBILITY IN FUSED SALT MIXTURES[1]

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In previous contributions[2] it has been shown that compound formation, solubility and ionization relationships in binary mixtures are fundamentally interdependent, and a number of general rules predicting qualitatively the stability of compounds, the divergence of solubility from the calculated ideal value, and the extent of ionization in polar solutions of various types have been formulated and tested. It has been established, in particular, that the primary factor controlling the amount of compound formation, the increase in solubility and the degree of ionization in systems of the type HX: RX is the diversity in character of the constituent radicals of the two components. A definite experimental criterion of this diversity is given, in the case of metallic radicals, by their position relative to hydrogen in the electrode potential series. It is found, for example,[3] that in a pure acid (such as sulfuric or formic acid) the corresponding salts of metals far removed from hydrogen in the electrode potential series (such as the alkali metals above, or silver below) show extensive acid salt formation, abnormal solubility and high conductivity. As hydrogen is approached from either side, the stability of complexes diminishes until no acid salts are isolable, solubility falls off practically to zero, and ionization decreases. Occasional discrepancies, however, have been noted, and it is certain that many other factors, although generally secondary in effect, must be taken into consideration before any strictly quantitative discussion of the subject can be attempted. Among the subsidiary factors which have already been indicated as significant may be mentioned unsaturation, atomic volume, valence, temperature and internal-pressure differences.

The first purpose of the present investigation was to test whether the rules deduced for systems of the type HX: RX could be extended to systems of the more general type RX_m: $R'X_n$. It was desired, in other words, to ascertain whether the diversity factor could be employed as a guiding principle for predicting the properties of *double salts* as well as those of

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[1] A condensation of theses submitted by E. D. Crittenden and H. K. Miller in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, August, 1922. Presented, in part, at the Pittsburgh Meeting of the American Chemical Society, September 6, 1922.

[2] See, particularly, (a) Kendall and Booge, THIS JOURNAL, **39**, 2323 (1917). (b) Kendall and Gross, *ibid.*, **43**, 1416 (1921). (c) Kendall, Davidson and Adler, *ibid.*, **43**, 1481 (1921).

[3] (a) Kendall and Davidson, THIS JOURNAL, **43**, 979 (1921). (b) Kendall and Adler, *ibid.*, **43**, 1470 (1921). (c) Kendall, Adler and Davidson, *ibid.*, **43**, 1846 (1921).

acid salts. The second object of the work was to study more intensively the several disturbing influences enumerated above. With those two points in mind, the fused salt mixtures used as experimental material were carefully selected in such a way as to vary all of the factors involved as widely as possible. From an examination of the results so obtained it was hoped that some disentanglement of the mutually obscuring effects of the different subsidiary factors would be feasible, although it was recognized that the complexity of the field necessarily precluded any but preliminary generalizations being drawn at this stage.

As the first component of each system studied, a reference salt of very slight polarity and with a conveniently low melting point was chosen. Three such salts were employed in all, namely, aluminum bromide, aluminum chloride and antimony trichloride. In combination with each of these, salts containing a common negative radical were taken as second components, the positive radical of the salts so selected being varied to the utmost. Three complete series of systems of the type $RX_m:R'X_n$ were thus secured, and the determination of their freezing-point curves has supplied the necessary data for establishing the dependence of compound formation and solubility relationships upon the nature of the radicals R and R'. Conductivity measurements upon the same systems will be presented and discussed in a subsequent paper.

In spite of the considerable quantity of work on double and complex salts recorded in the literature, very few of the systems examined by previous investigators are of value for comparison with the results here obtained. In some instances, compounds have been claimed to exist on obviously inadequate experimental grounds;[4] in others, experiments have been conducted throughout in aqueous solution, and the ternary compounds reported are not in general comparable.[5] No systematic study of fused salt mixtures, such as described in this article, has hitherto been undertaken, a rather strange fact in view of the recognized importance of the field. It is true that several fairly extensive series of fused chloride mixtures have recently been examined by various investigators[6] by the same freezing-point curve method here employed, but the selection of the components in almost every system included has been conspicuously unfortunate from the present viewpoint, salts of the same general character being run against one another and the variation in the different factors mentioned above being reduced to a minimum. It is of interest to note that the consequent scarcity of compounds obtained from these systems

[4] See, for example, Baud, *Ann. chim. phys.*, [8] **1**, 8 (1904).

[5] Compare Kendall and Davidson, THIS JOURNAL, **43**, 2131 (1921).

[6] Such as (a) Zemczuzny and Rambach, *Z. anorg. Chem.*, **65**, 403 (1910). (b) Hermann, *ibid.*, **71**, 257 (1911). (c) Menge, *ibid.*, **72**, 162 (1911). (d) Sandoninni, *Gazz. chim. ital.*, **44**, (I) 290 (1914).

has been so extreme as to excite special comment. In the systems recorded below, on the other hand, not only has confirmation been obtained for a number of compounds previously reported, but no fewer than 49 new "double salts" have been isolated.

Experimental Part

Owing to the extremely hygroscopic nature of the reference substances selected, the open-tube method preferred in previous work was here impracticable; and it was necessary to carry out all freezing-point determinations in sealed bulbs. A small bulb of 1- to 2cc. capacity was blown at the end of a Pyrex glass tube. The tube was weighed, a suitable amount of the second component added, and the tube weighed again. The reference salt was then introduced into the bulb from a weighing bottle and the tube immediately sealed with the aid of a blast lamp, leaving as little air space as possible. From the final weight of the tube the molecular percentages of the two salts present were calculated. After a little practice the quantities necessary to make up a mixture of any required composition could be judged without much difficulty, and a representative set of bulbs was thus obtained for each system.

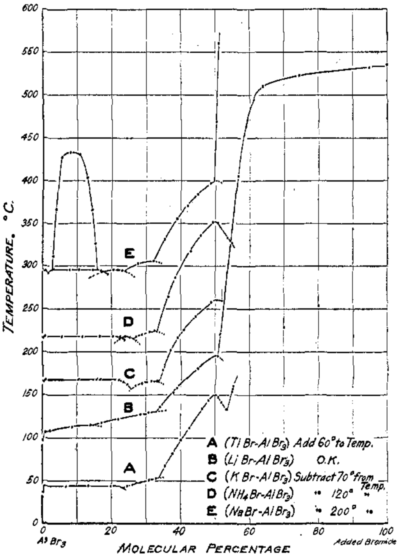

Fig. 1.

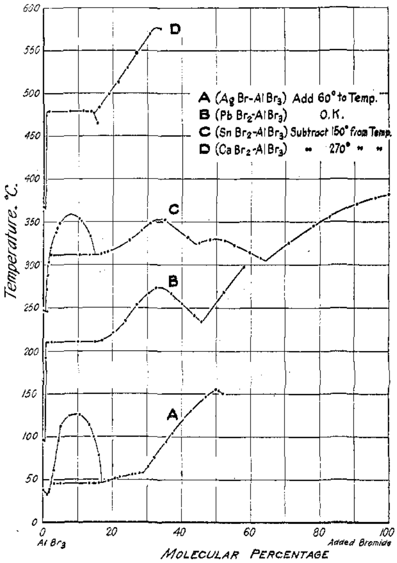

Fig. 2.

The freezing point of each mixture was determined by immersing the tube in a bath well above the temperature necessary for complete fusion, shaking thoroughly to ensure homogeneity of the melt, cooling till crystallization was induced, and then transferring to a bath the temperature of which was raised very slowly (not more than 0.2° per minute) until, under constant agitation, the last trace of crystals disappeared. For minor details of procedure, reference should be made to earlier articles.

The baths employed, with their respective temperature ranges, were as follows: solid carbon dioxide–alcohol (—40° to —20°); fuming nitric acid–ice (—20° to —10°); salt-ice (—10° to 0°); water (0° to 80°); sulfuric acid (30° to 110°); ammonium sulfate—sulfuric acid[7] (110° to 200°); potassium nitrate—sodium nitrate—calcium nitrate[8] (200° to 310°); and sodium nitrate—potassium nitrate (310° to 550°). Four thermometers were used, all graduated in 0.1°, covering ranges from —40° to +25°, 0° to 100°, 100° to 200°, and 200° to 300°, respectively. Temperatures above 300° were measured by means of a base metal pyrometer with a low-resistance, direct-reading galvanometer. The thermometers and pyrometer were standardized at 10° intervals by comparison with a platinum resistance thermometer,[9] carefully calibrated at the freezing and boiling points of water and at the boiling point of sulfur according to the method prescribed by the Bureau of Standards.[10] The thermometers were always immersed to a fixed depth during determinations and, the conditions throughout the calibration being made the same, no further corrections were necessary.

The freezing point of each mixture was checked at least twice. The precision of measurement varied considerably in different systems (and even in different regions of the same system) according to the slope of the freezing-point curve, but the approximate limits of accuracy may be stated as follows: below —10°, 0.5° to 1.0°; between —10° and 100°, 0.3° to 0.5°; between 100° and 200°, 0.5° to 1.0°; between 200° and 300°, 1.0° to 2.0°; between 300° and 550°, 2.0° to 5.0°. The higher limits may be considered as referring to the *accuracy* of the temperature measurements, taking into account all probable sources of error, that is, constant and personal errors as well as errors of method. The lower limits express the *reproducibility* of the experimental values.

The compositions of the various mixtures, given throughout in molecular percentages, are accurate in general to 0.1%. The filling and sealing of the bulbs were restricted entirely to exceptionally cold, dry days, in order to reduce as far as possible the action of water vapor upon the salts during the short interval of exposure.

Preparation of Reference Salts.—For the preparation of aluminum bromide, 30-mesh C. P. aluminum was thoroughly washed with alcohol and added gradually to

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[7] Kendall and Landon, THIS JOURNAL, **42**, 2133 (1920).

[8] Menzies and Nutt, *ibid.*, **33**, 1366 (1912).

[9] For the use of this thermometer and accessories we are indebted to Professor C. D. Carpenter of this Department.

[10] *Bur. Standards Sci. Paper*, **124** (1909). Mueller and Burgess, THIS JOURNAL, **41**, 748 (1919).

bromine. When the reaction subsided, an excess of aluminum was added, and the product was digested over a low flame for an hour. The pure salt was then obtained by several distillations from the excess of aluminum, followed by sublimation at 105°. Only small quantities were sublimed at a time, since the salt, which is perfectly white at first, is very readily affected by exposure to the air or to traces of moisture, becoming light yellow in color. All samples used in this work were freshly prepared, and were kept in a clean, dry weighing bottle over phosphoric anhydride in a vacuum desiccator before being transferred to the bulbs. The melting points of several samples were quite uniform at 97.1°, a value considerably higher than any previously recorded.[11]

Aluminum chloride was prepared by passing washed and dried hydrogen chloride over heated aluminum powder, the product being sublimed directly into a weighing bottle and all precautions taken to ensure the absence of water. A practically colorless product was obtained, melting sharply at 190.2°.

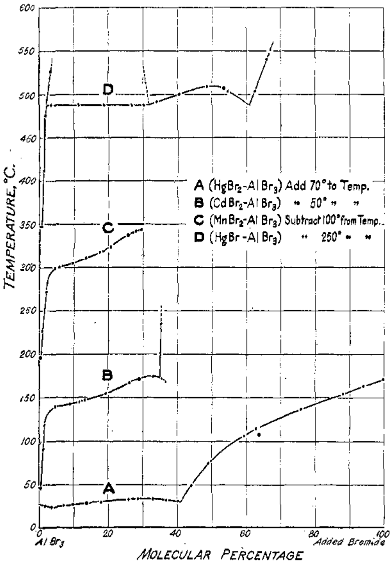

Fig. 3.

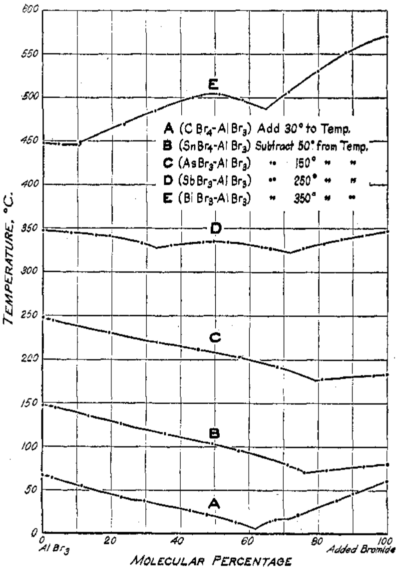

Fig. 4.

Antimony trichloride was made through the pentachloride, prepared by passing chlorine over lumps of metallic antimony and then reduced by digestion with an excess of powdered metal. Fractional distillation gave a clear product boiling at 232–234°, which was further purified by sublimation at 100°. The pure white crystals melted sharply at 73.4°.

Any special points in the preparation of the second components of the various mixtures will be mentioned under their particular systems below. The freezing-point data are tabulated as in previous work, *T* denoting the temperature of final disappearance of the solid phase. In the majority of systems many more points were determined than are tabulated below, but in order to save space only sufficient observations are included to establish the essential features of each freezing-point curve. The details of the more complex systems will be readily apprehended from the accompanying diagrams.

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[11] Richards and Krepelka [THIS JOURNAL, **43**, 2221 (1920)] have prepared this salt for atomic weight determinations by a much more elaborate method, but do not report the melting point of their product.

In those cases where the freezing-point curve rose to high temperatures (above 300°) while the comparatively volatile reference salt was still in excess, the pressure inside the bulbs necessarily became so high as to invite explosions. After a few minor casualties had been sustained, the attempt to complete such systems was abandoned. Fortunately, the last break in the diagram had already occurred, in most instances, before this danger zone was approached, and the solid phase separating from the last few mixtures examined could be definitely identified as the pure second component.

The order of presentation in each series below is based, for convenience, upon the position of the second component in the periodic system. Representative members of each group, wherever it was feasible to carry out determinations, are considered in turn.

Series I. Systems Containing Aluminum Bromide as Reference Salt

1. Lithium Bromide.—Pure lithium bromide was prepared from a C. P. sample by precipitating the carbonate, redissolving in the minimum quantity of hydrobromic acid, evaporating the solution and crystallizing it. The hydrated crystals obtained were freed from mother liquor, transferred to a small Pyrex tube, heated gently to drive off all water and then heated more strongly to 600°. The resulting salt was free from sodium and perfectly neutral in aqueous solution. Being highly hygroscopic, it was kept in a glass-stoppered bottle in an air oven at 120°.

No previous work on this system is recorded.

% LiBr	0.62	2.0	4.3	8.7	11.1	14.0	16.2	17.1	22.0
T	107.2	108.2	109.8	112.4	113.6	114.6	113.0	117.7	121.9
Solid phase	$7AlBr_3.LiBr$							$2AlBr_3.LiBr$	
	25.7	27.8	28.7	30.6	34.2	37.9	39.1	40.7	44.9
	125.2	126.7	127.9	129.4	135.5	152.2	157.9	164.5	180.7
	$2AlBr_3.LiBr$				$AlBr_3.LiBr$				
	46.8	48.4	50.6	51.4	56.7	63.9	74.6	90.0	100.0
	186.7	192.5	195.4	221.4	405.0	510.0	523.0	532.0	535.0
	$AlBr_3.LiBr$			LiBr					

2. Sodium Bromide.—The salt used was carefully recrystallized from a C. P. sample and dried at 120°.

Isbekow and Plotnikow[12] have reported that mixtures in this system containing low percentages of sodium bromide break up into 2 liquid layers, with a critical temperature of mixing near 230°, but isolated no compounds.

% NaBr	0.7	0.9	1.4	1.7	1.9	2.2	3.1	4.0	5.4
T	95.2	94.8	93.6	93.0	93.9	94.6	110.9^a	166.4^a	227.1^a
Solid phase	$AlBr_3$			$xAlBr_3.yNaBr$					
	7.8	10.4	12.8	14.5	15.3	17.0	17.7	18.4	19.0
	231.9^a	230.5^a	202.7^a	166.9^a	125.6^a	94.2	93.0	91.6	90.4
	$xABr_3.yNaBr$								
	16.9	18.4	20.5	21.5	22.1	23.4	24.0	25.1	27.5
	92.8	94.0	95.4	95.8	96.0	95.1	94.8	98.2	102.4
	$7AlBr_3.2NaBr$						$2AlBr_3.NaBr$		

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[12] Isbekow and Plotnikow, *Z. anorg. Chem.*, **71**, 328 (1911).

31.9	32.6	35.3	36.8	38.9	42.0	45.0	48.6	50.3
104.5	108.8	131.2	141.5	154.8	170.4	184.0	196.4	200.5
	AlBr$_3$.NaBr							
50.3	51.1							
269.0	360.0							
NaBr								

[a] Coalescence temperatures in a 2 liquid layer region extending from 2.6 to 16.3% of sodium bromide, and in equilibrium with solid phase xAlBr$_3$.yNaBr at 95.4°. Critical solution point 232° at 8.0% of sodium bromide.

3. Potassium Bromide.—Isbekow and Plotnikow obtained a 2 liquid layer region for this system also, but the critical solution temperature was too high for exact determination (over 360°). Weber[13] reported the formation of an equimolecular compound.

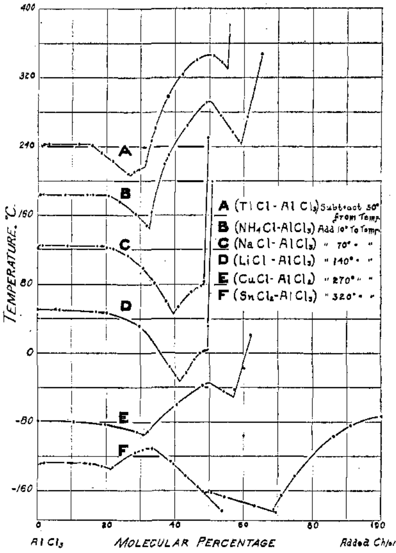

Fig. 5.

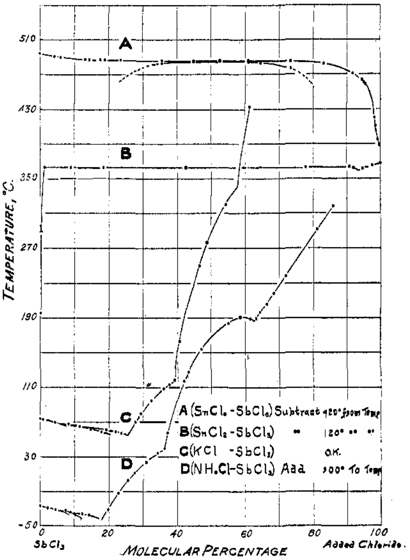

Fig. 6.

% KBr	0.33	0.86	19.4	23.3	24.7	25.8	27.1	28.8	31.6
T	97.5	265.9[a]	189.6[a]	95.6	92.2	88.6	90.8	93.0	95.5
Solid phase	xAlBr$_3$.yKBr					2AlBr$_3$.KBr			
	33.2	34.7	37.3	39.5	41.0	44.5	47.4	49.0	51.3
	95.8	109.0	130.6	145.9	154.6	171.4	181.7	188.4	189.6
		AlBr$_3$.KBr							
	52.0	54.7							
	188.8	>390.0							
	KBr								

[a] Coalescence temperatures in 2 liquid layer region extending from 0.4 to 22.1% of potassium bromide and in equilibrium with solid phase xAlBr$_3$.yKBr at 98.1°. The critical solution point and coalescence temperatures for intermediate mixtures lie too high for determination.

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[13] Weber, *Pogg. Ann.*, **103**, 259 (1858).

4. Ammonium Bromide.—Isbekow and Plotnikow found that this salt exhibited exactly the same behavior in aluminum bromide as the potassium salt.

% NH_4Br	T	Solid phase
0.52	160.5[a]	$xAlBr_3.yNH_4Br$
0.80	236.5[a]	
20.4	159.5[a]	
24.0	94.8	
22.8	96.6	$3AlBr_3.NH_4Br$
23.1	96.9	
23.8	97.5	
25.2	97.3	
27.3	92.7	
27.3	98.1	$2AlBr_3.NH_4Br$
28.2	99.9	
31.0	103.2	
32.4	103.8	
32.9	104.0	
33.5	103.6	
36.3	143.8	$AlBr_3.NH_4Br$
38.5	166.1	
43.0	197.2	
46.1	214.0	
49.5	230.5	
50.7	229.8	
53.4	213.6	
54.7	207.5	
57.1	360.0	NH_4Br

[a] Coalescence temperatures in a 2 liquid layer region extending from below 0.5 to 20.8% of ammonium bromide, and in equilibrium with the solid phase $xAlBr_3.yNH_4Br$ at 98.0°.

5. Silver Bromide.—This salt was prepared by precipitation from a solution of c. p. hydrobromic acid with silver nitrate in a dark room, repeated washing, careful drying at 120° and then heating to 200°. The material was kept in the dark and all bulbs made up and examined in red light as far as possible, to avoid decomposition.

Isbekow and Plotnikow have found that this system behaves similarly to that of sodium,[14] a 2 liquid layer region with a critical temperature of mixing of 180° being obtained.

% AgBr	T	Solid phase
1.1	94.2	$AlBr_3$
1.3	93.4	
1.5	95.3	$2AlBr_3.AgBr$
1.6	98.2	
3.0	120.4[a]	
4.5	156.3[a]	
5.0	161.9[a]	
7.6	183.6[a]	
13.4	173.0[a]	
14.7	159.7[a]	
16.2	139.7[a]	
18.7	108.6	
20.7	111.3	
22.1	112.8	
25.6	115.6	
26.4	116.9	
27.8	117.8	
30.2	125.2	$AlBr_3.AgBr$
32.0	135.0	
35.6	154.6	
37.3	164.1	
39.2	174.1	
40.9	182.3	
42.7	189.5	
46.8	206.8	
50.2	215.8	
50.6	214.2	
52.0	210.3	
54.9	319.0	AgBr

[a] Coalescence temperatures in a 2 liquid layer region extending from 2.2 to 17.0% of silver bromide, and in equilibrium with solid phase $2AlBr_3.AgBr$ at 105.9°. The critical solution point is 186° at 9.8% of silver bromide.

6. Calcium Bromide.—Recrystallization from a u. s. p. sample gave the hexahydrate. This was carefully decomposed by gentle heating and the product, after being dried in an oven at 120°, was fused in a Pyrex tube to ensure complete removal of water. The final material was practically neutral in aqueous solution.

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[14] The close resemblance of sodium and silver systems on the one hand, and of potassium and ammonium systems on the other, has been noted several times in previous articles of this series. See, for example, Ref. 3a, p. 987.

% $CaBr_2$	0.74	15.4	16.0	18.9	21.4	24.3	27.3	30.9	33.8	33.8
T	204.2[a]	195.3	213.1	229.5	242.6	260.1	276.8	298.4	304.9	398.0
Solid phase	$x\mathrm{AlBr_3}.y\mathrm{CaBr_2}$		$2\mathrm{AlBr_3}.\mathrm{CaBr_2}$							$CaBr_2$

[a] A 2 liquid layer region extends from 0.8 to 14.0% of calcium bromide, in equilibrium with solid phase $x\mathrm{AlBr_3}.y\mathrm{CaBr_2}$ at 208.8°. Coalescence temperatures lie too high for determination.

7. Barium Bromide.—Isbekow and Plotnikow report that this salt is insoluble in aluminum bromide. The data presented below show this to be incorrect.

% $BaBr_2$	18.3	21.2	24.2	28.0
T	276.7[a]	292.0	310.0	335.0
Solid phase	$2\mathrm{AlBr_3}.\mathrm{BaBr_2}$(?)			

[a] A 2 liquid layer region extends from below 0.9 to 16.0% of barium bromide, in equilibrium with solid phase $2\mathrm{AlBr_3}.\mathrm{BaBr_2}$ at 269.4°. Coalescence temperatures lie too high for determination.

8. Magnesium Bromide.—The anhydrous salt was prepared from a c. p. sample of the hexahydrate by first forming the stable equimolecular compound with ammonium bromide, heating very gently to drive off all of the water, and then raising the temperature gradually until the compound $\mathrm{MgBr_2}.\mathrm{NH_4Br}$ was completely decomposed. The product obtained by continued ignition was quite free from ammonium salt, and practically neutral in aqueous solution. Attempts at direct dehydration of the hexahydrate always led to a highly basic material, owing to formation of oxide.

% $MgBr_2$	0.6	1.4	0.6	1.4	3.8	8.1	12.9	18.4	21.6	23.5	24.0
T	96.8	96.5	134.9	160.7	190.2	199.6	210.5	221.6	227.9	231.5	$>$360.0
Solid phase	$AlBr_3$		$2\mathrm{AlBr_3}.\mathrm{MgBr_2}$(?)								$MgBr_2$

9. Zinc Bromide.—A c. p. sample was recrystallized, dried at 120°, transferred to a bent Pyrex tube and distilled. The product obtained was extremely hygroscopic, and all precautions possible were taken to guard against contamination with water vapor before use.

Isbekow and Plotnikow report completely homogeneous solutions in this system. In the present work this was found to be due to supercooling. As much as 66% of zinc bromide could readily be brought into solution in aluminum bromide, but as the temperature was lowered a glass formed which refused to crystallize even after months of standing. This phenomenon rendered the determination of freezing points difficult even with small amounts of zinc bromide, and measurements could not be carried beyond 35%.

% $ZnBr_2$	2.6	5.6	11.3	14.5	11.3	12.1	14.5	20.6	26.7
T	95.5	94.4	87.6	83.5	95.1	96.1	99.3	104.1	108.8
Solid phase	$AlBr_3$				$2AlBr_3.ZnBr_2$				
	30.0	35.1							
	110.4	110.6							
	$2AlBr_3.ZnBr_2$								

10. Cadmium Bromide.—The salt used was a C. P. sample, recrystallized once and dried carefully at 120°.

% $CdBr_2$	0.7	1.1	1.8	4.5	5.2	9.0	11.6	13.0	19.3
T	95.6	140.7	168.1	189.6	190.0	192.9	195.4	197.0	204.2
Solid phase	$AlBr_3$	$2AlBr_3.CdBr_2$							
	26.0	28.9	33.1	35.3	35.3				
	217.4	221.2	224.0	223.1	234.9				
	$2AlBr_3.CdBr_2$				$CdBr_2$				

11. Mercurous Bromide.—The precautions observed in the preparation and preservation of this salt were similar to those described under silver bromide.

% HgBr	0.6	1.2	1.7	3.3	33.9	35.0	40.5	44.4	48.6
T	96.6	161.5	225.4	275.5[a]	242.1	243.9	250.1	255.1	259.7
Solid phase	$AlBr_3$	$AlBr_3.HgBr$							
	53.2	54.7	59.6	62.7	66.1				
	256.6	252.9	241.4	243.7	281.3				
	$AlBr_3.HgBr$			HgBr					

[a] The coalescence temperature in a 2 liquid layer region extending from 1.8 to 30.8% of mercurous bromide, and in equilibrium with solid phase $AlBr_3.HgBr$ at 238.1°.

12. Mercuric Bromide.—This salt was prepared by addition of bromine to mercury (kept under water to control the action) and purified by two recrystallizations. The carefully dried product melted sharply at 241.5°.

% $HgBr_2$	1.4	3.8	7.1	10.1	13.7	17.9	25.8	28.7	31.4
T	95.8	94.3	95.9	96.7	98.7	100.1	102.8	103.6	104.1
Solid phase	$AlBr_2$	$2AlBr_3.HgBr_2$ (stable modification)							
	32.8	37.7	40.3	4.6	7.1	9.8	17.9	20.1	25.8
	103.9	103.1	101.9	93.5	94.7	95.8	99.1	100.1	101.9
				$2AlBr_3.HgBr_2$ (metastable modification)					
	28.7	32.2	40.3	44.2	45.2	49.4	59.6	62.8	75.7
	102.5	102.6	100.7	118.8	123.2	145.5	175.0	183.6	206.8
				$HgBr_2$					
	83.1	88.0	94.0	98.1	100.0				
	217.1	224.4	232.9	239.1	241.5				
	$HgBr_2$								

13. Thallous Bromide.—The precipitate obtained by adding a solution of C. P. hydrogen bromide to pure thallous sulfate was thoroughly washed, dried at 120° and heated to 200° to ensure the decomposition of any acid salt.

% TlBr	0.6	21.4	22.4	24.4	24.4	26.0	26.9	28.4	30.7
T	260.0^a	260.0^a	118.4^a	99.9	104.4	105.9	106.7	108.1	110.6
Solid phase	xAlBr$_3$.yTlBr					2AlBr$_3$.TlBr			
	32.7	35.4	37.6	40.0	40.7	42.2	46.3	48.2	51.0
	111.8	126.8	142.1	157.7	160.4	171.8	192.9	203.4	207.9
						AlBr$_3$.TlBr			
	52.1	53.3	55.0	55.2					
	200.8	193.1	213.8	215.9					
	AlBr$_3$.TlBr		TlBr						

^{a} Coalescence temperatures in a 2 liquid layer region extending from below 0.6 to 22.8% of thallium bromide. and in equilibrium with solid phase xAlBr$_3$.yTlBr at 103.9°.

14. Carbon Tetrabromide.—A museum specimen was recrystallized from absolute alcohol and dried in a vacuum. The final product melted sharply at 90.1°

% CBr$_4$	0.0	1.0	2.7	11.5	23.0	29.5	42.5	47.6	49.5	55.9
T	97.1	96.6	94.5	85.7	72.5	68.5	56.7	52.3	50.2	44.0
Solid phase	AlBr$_3$ (α modification)					AlBr$_3$ (β modification)				
	66.1	67.6	73.7	85.5	90.3	100.0				
	44.7	46.1	51.7	68.8	77.6	90.1				
	CBr$_4$ (β modification)		CBr$_4$ (α modification)							

15. Stannous Bromide.—The bright yellow solution obtained by the action of c. p. hydrobromic acid on 30-mesh tin was evaporated to small bulk, and crystals of a hydrated complex acid salt separated. These were freed from mother liquor on a porous plate, transferred to a Pyrex tube, and heated carefully to drive off all water and hydrogen bromide. Samples from 2 different preparations melted sharply at 232°; the best previously recorded value[15] is 215.5°.

% SnBr$_2$	0.35	0.81	1.07	0.81	1.07	1.45	2.1	3.4	4.7
T	96.9	96.5	96.3	121.6	137.1	152.8	169.1^a	187.3^a	198.0^a
Solid phase	AlBr$_3$					2AlBr$_3$.SnBr$_2$			
	10.4	10.7	13.3	16.4	16.6	18.5	24.7	28.3	30.7
	202.4^a	201.4^a	185.4^a	162.2	162.7	164.3	178.5	190.2	197.8
				2AlBr$_3$.SnBr$_2$					
	34.9	41.5	43.7	44.8	48.3	52.4	55.2	59.6	62.8
	202.0	181.8	175.4	175.0	179.8	179.1	172.9	164.4	158.3
	2AlBr$_3$.SnBr$_2$					AlBr$_3$.SnBr$_2$			
	71.2	78.1	82.9	90.8	96.2	100.0			
	175.1	195.9	206.4	220.9	228.2	232.0			
			SnBr$_2$						

^{a} Coalescence temperatures in a 2 liquid layer region extending from 1.8 to 14.2% of stannous bromide, and in equilibrium with solid phase 2AlBr$_3$.SnBr$_2$ at 161.1°. The critical solution point is 204.5° at 8.4% of stannous bromide.

16. Stannic Bromide.—This salt was prepared by the direct action of bromine on powdered tin. By two distillations from an excess of metal beautiful white crystals were obtained, melting sharply at 31.0°.

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[15] Abegg, "Handbuch der Anorganischen. Chemie," Part 2, **3**, 571 (1909), Hirzel.

% $SnBr_4$	1.9	2.5	13.4	22.7	35.4	49.2	56.7	71.2	74.4	76.0	82.5	93.3	100.0
T	96.0	94.3	85.4	76.4	65.7	53.7	45.8	29.7	25.5	22.3	23.4	27.6	31.0
Solid phase	$AlBr_3$ (α modification)				$AlBr_3$ (β modification)					$SnBr_4$			

17. Lead Bromide.—Lead tetrabromide is too unstable to be included in this work. The dibromide, however, was readily obtained pure by the method described under silver.

% $PbBr_2$	0.63	16.9	20.1	23.7	27.0	30.5	32.5	37.0	39.0	43.6	45.5	52.3	57.7
T	191.9[a]	211.9	220.4	235.5	253.5	267.7	272.5	266.9	257.0	241.6	234.9	268.4	296.8
Solid phase	$2AlBr_3.PbBr_2$											$PbBr_2$	

[a] A 2 liquid layer region extends from 0.8 to 16.2% of lead bromide, in equilibrium with solid phase $2AlBr_3.PbBr_2$ at 210.4°. Coalescence temperatures lie too high for determination.

18. Phosphorus Tribromide.—A c. p. sample was twice distilled and the middle fraction, boiling constantly at 175°, collected in tubes which were kept sealed until used. In spite of all precautions, however, bulbs containing more than 50% of phosphorus tribromide gave unsatisfactory results, probably due to contamination with traces of water during filling. When such bulbs were cooled, a fine mist of crystals (presumably phosphorus oxybromide) slowly deposited, and no reproducible freezing points could be obtained.

% PBr_3	7.3	14.4	22.4	31.5	44.0	48.2	49.1
T	91.3	84.1	76.6	67.3	53.6	47.0	45.4
Solid phase	$AlBr_3$ (α modification)			$AlBr_3$ (β modification)			

19. Arsenic Tribromide.—A very pure product, melting sharply at 32.8°, was obtained from a c. p. sample by two distillations, the middle fraction from the second distillation being preserved in a sealed tube.

% $AsBr_3$	5.3	19.3	32.8	40.1	44.8	46.4	56.9	68.0	80.9	96.1	100.0
T	94.5	81.1	69.5	65.7	61.9	60.9	52.8	41.7	28.2	32.2	32.8
Solid phase	$AlBr_3$ (α modification)		$AlBr_3$ (β modification)							$AsBr_3$	

20. Antimony Tribromide.—The method employed in the preparation of this salt was similar to that described for aluminum tribromide. Two distillations gave a product melting sharply at 96.6°, a value higher than any previously recorded.

% $SbBr_3$	8.2	15.2	19.2	28.6	37.1	46.5	49.3	53.5	63.5
T	94.7	92.3	90.3	82.9	80.5	84.2	85.1	84.3	78.8
Solid phase	$AlBr_3$				$AlBr_3.SbBr_3$				
	66.4	72.5	75.7	81.6	86.7	92.8	100.0		
	76.9	72.9	76.3	81.9	86.5	91.3	96.6		
		$SbBr_3$							

21. Bismuth Tribromide.—This salt was prepared by addition of bromine to metallic bismuth. An apparatus with reflux condenser was used because of the slowness of the reaction at temperatures below the boiling-point. The bright yellow product was gently heated to remove the last traces of free bromine, placed in a bent Pyrex tube and slowly distilled into the cooler part of the tube. The final samples melted uniformly at 220.4°, the best value reported in the literature hitherto being 215°.

% $BiBr_3$	4.4	10.6	10.6	23.6	32.5	43.5	46.0	51.1	57.7
T	96.8	95.5	98.5	119.2	135.5	150.2	152.0	153.1	147.8
Solid phase	$AlBr_3$		$AlBr_3.BiBr_3$						
	65.6	71.5	79.7	88.0	100.0				
	137.3	156.9	180.1	202.7	220.4				
		$BiBr_3$							

22. Chromic Bromide.—The direct action of bromine on heated chromium metal gave small quantities of black, shining crystals, which were identified as the tribromide. These were found to be practically insoluble in aluminum bromide, since a bulb containing 0.5% of the substance did not give a clear solution, even at 300°.

23. Manganous Bromide.—A c. p. sample was recrystallized from water and carefully heated to decompose the resulting hydrate. The salt was then fused and kept well protected against moisture until used.

% $MnBr_2$	0.68	0.68	1.98	4.6	5.6	9.4	13.8	17.5	20.6
T	96.3	127.1	171.6	199.1	199.8	204.6	210.8	217.6	223.8
Solid phase	$AlBr_3$	$2AlBr_3.MnBr_2$(?)							
	24.0	25.8	28.0	29.6	31.0				
	232.9	237.7	241.7	242.6	>300.0				
	$2AlBr_3.MnBr_2$(?)				$MnBr_2$				

24. Nickelous Bromide.—Anhydrous nickel bromide was obtained as a finely divided, deep brown powder by treating the metal with hydrobromic acid, recrystallizing the hydrate, and carefully heating to 250°.

Isbekow and Plotnikow report that nickelous bromide is completely insoluble in aluminum bromide. In this work it was found possible to bring 0.54% into solution at 300°, but 0.78% did not dissolve completely even after protracted heating at 360°.

25. Ferrous Bromide.—The product obtained by heating a c. p. sample gradually to 500° was of rather doubtful purity, and the formation of deeply colored solutions rendered the determination of exact melting points very difficult. This system was, therefore, only qualitatively examined. As far as ascertained, the curve strongly resembles those given by cadmium and manganous bromides. The limit of solubility at 300° is approximately 20%.

Series II. Systems Containing Aluminum Chloride as Reference Salt

26. Lithium Chloride.—Lithium carbonate was precipitated from a solution of C. P. lithium chloride by addition of ammonium carbonate. The precipitate, after repeated washing, was dissolved in hydrochloric acid, and the first crop of crystals obtained on evaporation carefully dried to constant weight. The final product was perfectly free from sodium and gave a neutral aqueous solution.

% LiCl	6.6	17.2	20.1	29.6	38.4	40.1	43.2	45.8	47.4	49.6	49.6	50.5
T	190.0	187.9	186.4	171.4	125.6	114.4	117.8	132.8	139.9	143.0	170.4	338.5
Solid phase	$AlCl_3$						$AlCl_3.LiCl$				LiCl	

27. Sodium Chloride.—This system has been previously investigated by Baud,[4] who reported 3 compounds. The methods he employed, however, are open to serious criticism, and only one of his compounds, the equimolecular, has here been confirmed.

% NaCl	20.1	22.1	26.1	30.6	33.9	37.3	41.1	44.8	47.6	48.3	48.4	49.5
T	192.0[a]	190.0	182.0	169.4	151.3	130.2	123.6	140.7	147.9	151.9	153.7	320.5
Solid phase	$xAlCl_3.yNaCl$						$AlCl_3.NaCl$				NaCl	

[a] A 2 liquid layer region extends from below 0.2 to 18.0% of sodium chloride, in equilibrium with solid phase $xAlCl_3.yNaCl$ at 193.5°. Coalescence temperatures lie too high for determination.

28. Potassium Chloride.—The work of Baud upon this system also proved unreliable, as only 1 of the 4 compounds which he reported was isolated.

% KCl	19.0	23.0	27.0	31.2	34.5	37.5	42.9	48.8	49.5	51.5
T	192.5[a]	187.4	177.2	162.1	158.4	178.7	213.1	248.4	255.5	375.0
Solid phase	$xAlCl_3.yKCl$				$AlCl_3.KCl$				KCl	

[a] A 2 liquid layer region extends from below 0.4 to 18.2% of potassium chloride, in equilibrium with solid phase $xAlCl_3.yKCl$ at 193.0°.

29. Ammonium Chloride.—The compound $AlCl_3.NH_4Cl$ reported by Baud is here confirmed.

% NH_4Cl	0.20	20.6	23.8	28.5	31.9	33.2	36.9	38.2	43.5
T	192.2	192.3[a]	186.6	171.8	157.9	173.4	229.4	239.7	274.1
Solid phase	$xAlCl_3.yNH_4Cl$					$AlCl_3.NH_4Cl$			
	49.1	53.1	56.8	58.4	61.0	65.1			
	301.2	287.2	266.1	257.1	284.3	357.0			
	$AlCl_3.NH_4Cl$				NH_4Cl				

[a] A 2 liquid layer region extends from 0.2 to 20.5% of ammonium chloride, in equilibrium with solid phase $xAlCl_3.yNH_4Cl$ at 192.5°.

30. Cuprous Chloride.—Copper turnings, hydrochloric acid and cupric chloride were warmed together until a colorless solution was obtained, and the mixture was then poured into dil. sulfurous acid. The cuprous salt precipitated was washed with sulfurous acid, glacial acetic acid, alcohol and ether, and dried to constant weight.

% $CuCl$	10.5	19.7	29.0	30.8	32.2	40.6	47.9	48.1	50.9
T	190.0	187.4	178.4	175.3	178.3	209.9	230.9	231.6	231.9
Solid phase	$AlCl_3$				$AlCl_3.CuCl$				
	54.0	57.4	60.1	62.0					
	225.9	227.4	252.5	291.5					
		$CuCl$							

31. Silver Chloride.—

% $AgCl$	0.38	20.1	26.5	32.6	33.4	38.0	39.7	39.9	43.6
T	191.2[a]	190.1	184.5	161.5	156.0	136.8	121.9	122.2	138.9
Solid phase	$xAlCl_3.yAgCl$							$AlCl_3.AgCl$	
	47.0	47.9	49.1	50.8					
	147.5	175.4	285.3	378.0					
		$AgCl$							

[a] A 2 liquid layer region extends from 0.7 to 17.6% of silver chloride, in equilibrium with solid phase $xAlCl_3.yAgCl$ at 192.9°.

32. Barium Chloride.—The anhydrous salt was obtained by carefully fusing the recrystallized C. P. dihydrate.

% $BaCl_2$	14.0	20.1	22.8	27.1
T	192.5[a]	198.8	209.4	255.5
Solid phase	$2AlCl_3.BaCl_2$(?)			

[a] A 2 liquid layer region extends from below 2.0 to 13.0% of barium chloride, in equilibrium with solid phase $2AlCl_3.BaCl_2$ (?) at 191.5°.

33. Magnesium Chloride.—A pure anhydrous sample was obtained through the double ammonium salt, as in the case of the bromide.

% $MgCl_2$	9.5	12.4	15.4	17.9	22.1	27.5	29.1	30.9
T	188.6	187.4	186.4	188.0	207.6	224.2	227.4	>350.0
Solid phase	$AlCl_3$			$2AlCl_3.MgCl_2$(?)				$MgCl_2$

34. Mercurous Chloride.—Work on this system had to be abandoned, since blackening of the mercurous chloride in bulbs containing low percentages and violent explosions in bulbs containing larger amounts prevented the determination of exact freezing points. Solubility is certainly only slight, and it is probable that no isolable compounds are formed.

35. Mercuric Chloride.—

% $HgCl_2$	3.0	7.7	18.5	26.4	32.8	37.4	41.4	48.2	55.9
T	190.0	189.7	189.0	184.6	177.5	167.5	167.4	151.3	192.0
Solid phase				$AlCl_3$					
	58.1	63.2	70.9	82.6	90.0				
	200.5	216.2	238.1	259.7	272.1				
			$HgCl_2$						

36. Thallous Chloride.—The method of preparation was analogous to that described in the case of the bromide.

% $TlCl$	0.52	0.90	15.6	18.7	21.8	26.1	28.2	29.2	31.4
T	189.4	189.9[a]	190.2	182.3	172.8	158.8	160.5	162.9	172.6
Solid phase	$AlCl_3$		$xAlCl_3.yTlCl$					$2AlCl_3.TlCl$(?)	
	33.1	34.2	37.9	42.1	46.2	51.2	53.5	55.5	56.5
	196.6	211.4	248.1	274.1	290.0	295.5	288.1	325.0	360.0
	$AlCl_3.TlCl$							$TlCl$	

[a] A 2 liquid layer region extends from 1.2 to 14.7% of thallium chloride, in equilibrium with solid phase $xAlCl_3.yTlCl$ at 192.0°.

37. Stannous Chloride.—Tin was digested with hydrochloric acid, and the crystals obtained by evaporation were purified by fusion and distillation in a bent Pyrex tube. The samples employed melted sharply at 246.8°.

% $SnCl_2$	0.98	1.11	15.3	18.1	22.1	28.5	30.7	33.5	38.8
T	191.0	191.3	191.0[a]	188.2	187.0	204.4	207.4	209.1	195.0
Solid phase		$xAlCl_3.ySnCl_2$					$2AlCl_3.SnCl_2$		
	43.1	47.1	48.5	53.9	50.7	54.6	63.5	69.8	68.5
	178.6	164.1	158.7	136.9	158.2	153.3	142.3	135.4	138.3
	$2AlCl_3.SnCl_2$					$AlCl_3.SnCl_2$			
	70.9	75.0	86.1	90.8	100.0				
	154.3	176.3	223.4	235.7	246.8				
			$SnCl_2$						

[a] A 2 liquid layer region extends from 1.5 to 14.3% of stannous chloride, in equilibrium with solid phase $xAlCl_3.ySnCl_2$ at 192.0°

38. Stannic Chloride.—A stream of purified chlorine was passed over melted tin, and the product redistilled from the excess of metal. A colorless product was obtained which was free from uncombined chlorine, boiled at 114° and solidified at —30.2°.

% $SnCl_4$	6.8	19.3	34.8	47.3	53.8	63.2	74.4	83.4	89.6
T	188.6	182.6	174.2	167.8	164.5	158.3	150.0	139.5	130.9
Solid phase					$AlCl_3$				
	93.2	95.9	98.8	99.6	100.0				
	122.0	113.4	89.9	65.7	−30.2				
		$AlCl_3$			$SnCl_4$				

39. Antimony Chloride.—

% $SbCl_3$	3.6	17.1	21.9	32.2	41.4	46.7	52.2	59.5	64.2
T	190.0	188.6	186.9	181.6	173.6	168.4	160.7	147.6	137.3
Solid phase	$AlCl_3$								

% $SbCl_3$	74.4	77.0	84.8	92.5	95.9	100.0
T	112.9	106.1	83.0	69.9	71.1	73.4
Solid phase	$AlCl_3$			$SbCl_3$		

40. Chromic Chloride.—Bulbs containing less than 1.0% of sublimed c. p. chromic chloride, in the form of glistening purple crystals, showed no trace of solution even after long heating at 300°.

41. Manganous Chloride.—A c. p. sample of hydrated salt was carefully dehydrated and fused in a Pyrex tube.

% $MnCl_2$	8.4	9.7	13.5	16.1	19.1	20.9	23.5	31.4	32.4
T	190.0	189.9	186.4	185.4	197.2	203.9	212.9	226.9	271.1
Solid phase	$AlCl_3$				$2AlCl_3.MnCl_2$(?)				

% $MnCl_2$	34.9
T	308.8
Solid phase	$MnCl_2$

Series III. Systems Containing Antimony Trichloride as Reference Salt

42. Lithium Chloride.—It was not possible to obtain a curve for this system, since bulbs containing even less than 0.6% of lithium chloride did not give a clear solution at 300°.

43. Sodium Chloride.—The compound $SbCl_3.3NaCl$ has been reported[16] from work in aqueous solution. In absence of water, however, sodium chloride was found to be practically insoluble in antimony trichloride even at 300°.

44. Potassium Chloride.—The existence of three compounds, $SbCl_3.2KCl$, $3SbCl_3.7KCl$ and $SbCl_3.3KCl$, has been claimed by previous workers.[16] None of these was here confirmed, although 2 other compounds are indicated by the freezing-point diagram. Potassium chloride, unlike the corresponding lithium and sodium salts, is abundantly soluble in antimony chloride.

% KCl	0.74	1.6	4.4	5.0	5.5	6.4	8.7	11.8	12.3
T	72.4	71.8	69.8	69.2	68.9	68.3	67.4	64.6	64.1
Solid phase	$SbCl_3$ (α modification)						$SbCl_3$ (β modification)		

% KCl	15.0	18.0	19.0	22.2	23.8	28.0	29.5	32.6	36.2
T	62.0	59.2	60.3	58.0	57.0	69.8	79.7	94.8	109.4
Solid phase			$SbCl_3$ (γ modification)			$SbCl_3.KCl$			

% KCl	37.9	39.2	41.0	46.8	48.8	54.7	58.5	61.7	68.7
T	113.3	118.3	162.5	250.5	277.1	320.0	360.0	433.5	533.0
Solid phase		$2SbCl_3.3KCl$(?)					KCl		

45. Ammonium Chloride.—In this system, too, 3 compounds, $SbCl_3.NH_4Cl$, $SbCl_3.2NH_4Cl$ and $SbCl_3.3NH_4Cl$, are reported in the literature.[16]

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[16] Ref. 15, vol. 3, p. 589 (1907).

The existence of only the first of these was confirmed in this work, but a new compound, $2SbCl_3.3NH_4Cl$, was isolated.

% NH_4Cl	2.1	2.6	4.4	6.6	7.5	8.2	7.3	7.5	8.9
T	71.3	70.8	69.7	68.1	67.5	66.5	68.2	68.0	66.6
Solid phase			$SbCl_3$ (α modification)					$SbCl_3$ (β modification)	
	9.9	12.5	14.1	18.1	19.8	22.9	25.5	27.6	31.3
	65.7	64.4	63.1	59.5	70.0	89.2	104.1	110.6	123.1
			$SbCl_3$ (γ modification)				$SbCl_3.NH_4Cl$		
	34.7	36.2	37.2	42.2	43.2	47.4	55.3	58.9	61.7
	134.8	139.7	157.4	217.8	228.6	253.5	284.3	290.5	289.5
	$SbCl_3.NH_4Cl$					$2SbCl_3.3NH_4Cl$			
	63.5	64.6	66.7	68.7	72.2	81.3	85.9		
	289.5	296.8	305.8	318.0	338.5	392.0	418.0		
				NH_4Cl					

46. Cuprous Chloride.—A bulb containing less than 0.3% of this salt did not give a clear solution even after protracted heating at 300°.

47. Silver Chloride.—This salt is also practically insoluble (less than 0.2% at 300°) in antimony trichloride.

48. Barium Chloride.—A bulb containing below 0.4% did not show complete solution at 300°.

49. Mercurous Chloride.—This salt is slightly soluble in antimony trichloride; bulbs containing 0.42 and 0.61% gave clear solutions at 74° and 235°, respectively. With 2.0%, however, complete solution could not be obtained at 300°.

50. Mercuric Chloride.—

% $HgCl_2$	2.0	3.3	5.2	6.5	8.3	9.8	13.1	25.4	44.3
T	72.6	71.9	85.4	101.7	114.8	126.3	142.1	183.5	218.8
Solid phase	$SbCl_3$					$HgCl_2$			
	49.3	58.4	69.6	79.6	86.1				
	225.6	234.5	246.4	257.1	264.2				
			$HgCl_2$						

51. Aluminum Chloride.—This system has already been described in Series II.

52. Stannous Chloride.—

% $SnCl_2$	0.10	0.71	0.85	91.7	92.7	94.7	97.9	100.0
T	74.9	169.0	174.9	242.1[a]	240.7	241.3	244.5	246.8
Solid phase			$xSbCl_3.ySnCl_2$				$SnCl_2$	

[a] A 2 liquid layer region extends from 1.4 to 91.2% of stannous chloride, in equilibrium with solid phase $xSbCl_3.ySnCl_2$ at 243.1°.

53. Stannic Chloride.—

% $SnCl_4$	4.6	6.2	13.5	14.6	17.8	19.1	23.9	35.8	35.8
T	70.9	69.4	67.7	67.4	67.0	66.8	66.5	66.3	62.9[a]
Solid phase					$SbCl_3$				

45.2	45.2	52.9	52.9	61.1	61.1	64.8	64.8	99.7
66.1	65.9[a]	66.0	65.4[a]	65.9	64.5[a]	65.8	63.0[a]	−30.5
				$SbCl_3$				
99.7	100.0							
−30.5	−30.2							
	$SnCl_4$							

[a] Coalescence temperatures in a metastable 2 liquid layer region were observed between 35.8 and 73.5% of stannic chloride.

Review of Results

A. Aluminum Bromide Series.—In the 25 systems examined, 34 compounds have been established. Only 6 of the substances selected as second components gave no isolable compounds with aluminum bromide, the carbon tetrabromide, tin tetrabromide and arsenic tribromide (presumably also phosphorus tribromide) systems showing simple eutectics, while chromic bromide and nickelous bromide are practically insoluble.

The results obtained in the case of the 19 remaining systems are summarized in Table I. To save repetition of formulas, only the molecular proportions of the 2 components are therein indicated; thus, in the lithium bromide system, 7–1 indicates the compound $7AlBr_3.LiBr$. Melting points are added in parentheses in each instance where the compound is stable at its maximum, or where only a slight extrapolation on the freezing-point curve is necessary to fix this maximum. A question mark signifies that the composition of the compound is not definitely given by its own diagram, but can be deduced without much chance of error by comparison

Table I

Aluminum Bromide Systems

Number of system	Second component	Compounds isolated, with melting points
1	LiBr	7-1 (114.8°), 2-1, 1-1 (197°)
2	NaBr	*x–y*, 7-2 (95.6°), 2-1, 1-1 (201°)
3	KBr	*x-y*, 2-1 (95.8°), 1-1 (191.5°)
4	NH_4Br	*x–y*, 3-1 (97.8°), 2-1 (104.2°), 1-1 (232°)
5	AgBr	2-1, 1-1 (215.6°)
6	$CaBr_2$	*x–y*, 2-1 (306°)
7	$BaBr_2$	2-1 (?)
8	$MgBr_2$	2-1 (?)
9	$ZnBr_2$	2-1 (111.5°)
10	$CdBr_2$	2-1 (224°)
11	HgBr	1-1 (261°)
12	$HgBr_2$	2-1 (2 modifications; 103.9° and 102.8°)
13	TlBr	*x–y*, 2-1 (112°), 1-1 (210°)
15	$SnBr_2$	2-1 (205°), 1-1 (183°)
17	$PbBr_2$	2-1 (274°)
20	$SbBr_3$	1-1 (85.2°)
21	$BiBr_3$	1-1 (153.5°)
23	$MnBr_2$	2-1 (?)
25	$FeBr_2$	2-1 (?)

with systems of similar character. The compounds marked *x–y* will be discussed below.

B. Aluminum Chloride Series.—In this series 16 systems have been studied and 19 compounds isolated. The 11 systems from which positive results were obtained are listed in Table II, which gives the formulas of the compounds and their melting points, where stable. The mercuric chloride, tin tetrachloride and antimony trichloride systems led to simple eutectics, while chromic chloride and mercurous chloride are insoluble in aluminum chloride.

C. Antimony Trichloride Series.—Here 5 compounds have been gained from the 12 systems investigated. As will be seen from Table II, only 3 systems gave isolable double salts. The chlorides of lithium, sodium, copper (ous), silver, barium and mercury (ous) are practically insoluble in antimony trichloride. The mercuric chloride, aluminum chloride and tin tetrachloride diagrams show simple eutectics.

TABLE II

ALUMINUM CHLORIDE AND ANTIMONY TRICHLORIDE SYSTEMS

Number of system	Second component	Compounds isolated, with melting points	
		Series II ($AlCl_3$)	Series III ($SbCl_3$)
26, 42	$LiCl$	1–1 (143.5°)	....
27, 43	$NaCl$	*x–y*, 1–1	....
28, 44	KCl	*x–y*, 1–1	1–1, 2–3
29, 45	NH_4Cl	*x–y*, 1–1 (304°)	1–1, 2–3 (291°)
30, 46	$CuCl$	1–1 (233°)	....
31, 47	$AgCl$	*x–y*, 1–1	....
32, 48	$BaCl_2$	2–1 (?)	....
33	$MgCl_2$	2–1 (?)	....
36	$TlCl$	*x–y*, 2–1, 1–1 (297°)	....
37, 52	$SnCl_2$	*x–y*, 2–1 (209.3°), 1–1 (158.5°)	*x–y*
41	$MnCl_2$	2–1 (?)	....

Classification of Compounds.—Of the 57 compounds indicated, only 2 contain an excess of the second component.[17] These are the compounds $2SbCl_3.3KCl$ and $2SbCl_3.3NH_4Cl$. The equimolecular compounds number 20; 16 are of the type $RX_3.R'X$, 2 of the type $RX_3.R'X_2$, and 2 of the type $RX_3.R'X_3$. There are 21 compounds containing 2 molecules of reference salt to 1 of second component; 7 are of the type $2RX_3.R'X$ and 14 of the type $2RX_3.R'X_2$. Unique compounds of greater complexity are $3AlBr_3.NH_4Br$, $7AlBr_3.2NaBr$, and $7AlBr_3.LiBr$.[18] In 12 systems, finally, compounds of undetermined composition separate from 2 partially miscible liquid layers. This phenomenon is so unusual as to warrant a brief explanation.

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[17] Numerous double salts of this type recorded in the literature were not confirmed here.

[18] An analogous lithium compound of this type (Li_2SO_4, $7H_2SO_4$) has been reported in an earlier paper (Ref. 7, p. 2140).

Formation of Two Liquid Phases.—Immiscibility in the liquid state has seldom been noted in the fused salt mixtures previously studied.[19] Its common occurrence in the present investigation is to be ascribed, as will appear later, to the extreme internal pressure difference existent in many systems between the 2 components. In all of the 17 cases here observed, the solid phase in equilibrium with the two liquids at the freezing point is a *compound*. Two fundamentally distinct types of diagram, however, may be noted.

(*a*) *The 2 liquid layer region intersects only one branch of the freezing-point curve of the compound, and does not include its maximum.* Systems 5, 7, 11, 15 and 32 illustrate this type, examples of which are fairly plentiful in other fields.[20] The freezing-point curve sinks on one side of the 2 liquid region to a eutectic point, but rises on the other towards the maximum of the compound.

(*b*) *The 2 liquid layer region intersects both branches of the freezing-point curve of the compound and obliterates its maximum.* Previous systems of this type[21] are exceedingly rare, but no fewer than 12 new examples have here been found, namely, Systems 2, 3, 4, 6, 13, 27, 28, 29, 31, 36, 37 and 52. The freezing-point curve here falls away on *both* sides of the 2 liquid region to eutectic points, the maximum lying within the area of partial miscibility and, therefore, being indeterminable. The composition of the compound necessarily lies within the limits of the 2 liquid layer region, but cannot be ascertained definitely without direct analysis of the solid phase separating. This is not practicable in sealed bulb experiments, so that all compounds of this character are designated x–y in Tables I and II above. From the 2 liquid layer limits recorded for each system, the limiting ratios of x and y, however, may be calculated, and it is very probable that the lower ratio approximates closely, in most instances, to the actual composition of the compound.[22]

Allotropy.—One of the compounds discovered, namely $2AlBr_3.HgBr_2$, has been found to exist in 2 distinct crystalline modifications, melting at 103.9° and 102.8°, respectively.[23]

Aluminum bromide has also been found in 2 forms, with a transition point at 70.2°. This transition point was first indicated by breaks in the freezing-point curves of Systems 14, 16, 18 and 19, and was later confirmed with a sample of the pure salt by the thermal method.[24]

Antimony trichloride shows no less than 3 different crystalline modifica-

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[19] Compare Hildebrand, THIS JOURNAL, **38**, 1470 (1916).

[20] Roozeboom, "Heterogene Gleichgewichte," [2] **2**, 168–175 (1918).

[21] Ref. 20, pp. 175–181.

[22] Ref. 20, p. 177.

[23] To avoid confusion in the diagram for this system (Fig. 3, Curve A), only the points for the stable modification of the compound $2AlBr_3.HgBr_2$, are plotted.

[24] Ref. 20, 1, 114 (1901).

tions, with transition points at 69.5° and 65.0°. Breaks in the freezing-point curve at these two temperatures are evident in Systems 44 and 45, and were also obtained in the time-cooling curve of the pure salt.

Finally, the reported existence of carbon tetrabromide in 2 forms,[25] with a transition point at 48.4°, has here been confirmed.

Non-existence of Solid Solutions.—In previous work on fused salt mixtures, solid solutions have been quite commonly indicated by the curves.[26] The diagrams here obtained, however, do not exhibit a single example of solid solutions. It is true that the evidence is not entirely decisive, since complete solidus curves cannot be satisfactorily established from work on sealed bulbs. Nevertheless, observations upon temperatures of *incipient liquefaction* (first signs of softening of crystals) were carried out in many of the systems, and failed to indicate in any case that this temperature varied appreciably from the eutectic point. While, therefore, it is quite possible that in certain systems partial miscibility in the solid state may occur (the eutectics noted being, strictly speaking, eutectoids[27]), the extent of solid solution can be but small, and the conclusions drawn from the liquidus curves presented above must be substantially valid. The identity of the transition temperatures obtained for aluminum bromide and antimony trichloride in several systems with the values given by the pure salts is an additional argument against the existence of solid solutions. It is also important that the compounds obtained, in general, separated from solution in characteristic star-shaped needle clusters,[28] totally different in appearance from the crystals of the pure components.

Examination of the Factors Influencing Compound Formation and Solubility

1. The Diversity Factor.—When the results given in Tables I and II are examined in conjunction with the electrode-potential series of the metallic radicals[29] it is evident that in the field of fused salts, as in other fields previously studied, the generalization that compound formation and solubility depend primarily upon the diversity of the constituent radicals of the two components is still substantially valid, even although (as discussed in the introduction) the influence of the various subsidiary factors has here been intentionally accentuated. In Series I, for instance, the bromides of metals much more electropositive than aluminum (such as the alkali

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[25] Ref. 24, p. 127.

[26] Landolt-Börnstein, "*Physikalisch-Chemische Tabellen,*" **1912,** pp. 611–638.

[27] Clendinnen and Rivett [*J. Chem. Soc.*, **119,** 1337 (1921)] have recently emphasized the fact that *perfect* immiscibility in the solid state cannot exist. In most systems, however, it is certain that solid solution is so minute a factor as to be negligible.

[28] Compare Ref. 7, p. 2134.

[29] Ref. 14, p. 989. Abegg, Auerbach and Luther, *Abhandl. Deutsch. Bunsen Ges.* [5] **2,** (1911) and [8] (1915).

metals) provide the most complex and the most stable compounds. The bromides of the alkali earth metals exhibit fewer and more unstable double salts. Magnesium and zinc bromides show each a single compound very highly dissociated into its components on fusion, as evidenced by the remarkable flatness of the freezing-point curve. As we go further from aluminum down the series, compound formation again increases in extent, the cadmium, lead and tin systems furnishing compounds of ascending stability. Below hydrogen in the list the antimony, bismuth, mercury and silver systems give compounds stable at their maxima.

If the curves obtained are interpreted as solubility results, similar conclusions are reached in those cases where the freezing point of the second component is sufficiently above that of the reference salt to permit legitimate comparisons to be made. Thus the alkali bromides are all extremely soluble in aluminum bromide at temperatures only slightly above its melting point; at 130° the solubility lies between 30 and 40 mole percentage. With the bromides of the alkaline earth metals, solubility is less than 1 mole percentage at the same temperature. The magnesium, manganese, cadmium and lead systems also exhibit very low solubility values (less than 1%) at 130°. At the bottom of the list, however, silver bromide again shows a solubility exceeding 30 mole percentage.

Series II and III may be analyzed in like manner, although the data are here somewhat less extensive. Discrepancies certainly exist in all three series, as will be emphasized below, but the preponderant influence of the diversity factor is unmistakably evident throughout the whole work.

2. **The Valence Factor.**—It has been noted earlier[30] that whenever we compare two systems of the types, HX:RX and HX:R'X, in which the radicals R and R' have approximately *the same electrode potentials* but possess *different valence*, we find that compound formation and solubility are much less extensive in the case of the radical with the higher valence. Thus sodium sulfate forms more stable compounds with sulfuric acid than does barium sufate. Aluminum is more electropositive than zinc or ferrous iron (both of which form acid salts), but its sulfate gives no sign of compound formation with sulfuric acid; in fact it is practically insoluble.

Numerous confirmations of this valence rule are to be found in the systems of the type, $RX_m:R'X_n$, here studied. Systems in which the radical R' is univalent show, in general, several compounds, the unimolecular being particularly stable. Salts of divalent radicals seldom furnish more than one compound, and even that is sometimes unstable. Systems in which R' is trivalent give compounds in only two cases (Systems 20 and 21), and in each of these the shape of the curve indicates extensive dissociation in the liquid state. No compounds at all were obtained from those systems in which R' was quadrivalent.

[30] Ref. 14, p. 988.

A few specific examples may be cited. Sodium bromide gives 4 compounds (of which 2 are stable at their melting points) with aluminum bromide; barium bromide exhibits only one compound, and that is unstable. Silver bromide provides 2 compounds with the same reference salt, and mercuric bromide only one. Both silver chloride and cuprous chloride give stable compounds with aluminum chloride; mercuric chloride shows a simple eutectic.

3. The Unsaturation Factor.—When we examine the results for two systems in which the *same* element exhibits different valences, we find that the salt in which the radical is "unsaturated" shows far greater compound formation than the salt in which the maximum valence is exercised. Interesting comparsions are available in Tables I and II with mercurous-mercuric and stannous-stannic systems. Part of the difference in each case may be ascribed, of course, to the valence factor discussed immediately above, but that unsaturation itself influences compound formation and solubility very significantly may be seen by comparing other systems. Thus "unsaturated" lead bromide[31] and stannous bromide, in Series I, give much more extensive compound formation than the "saturated" mercuric salt, although lead and tin are closer than mercury to the reference radical aluminum. The exceptional stability of the compounds from the thallous salts in Systems 13 and 36 must also be regarded as due to their unsaturation counterbalancing the proximity of Tl^+ to Al^{+++} in the electrode-potential series.

4. The Position Factor.—Thus far we have considered the effect of varying the second component only, and have not examined what occurs as the reference salt is changed. When we do so, however, by comparing the results of Series I, II and III, we see that another factor must be taken into consideration. The two aluminum series are remarkably fertile in compounds, even those radicals nearest to aluminum in the electrode-potential series yielding positive results. The antimony series, on the other hand, is almost barren, even the chlorides of metals so far removed as lithium and sodium being practically insoluble in antimony trichloride. This is particularly surprising when it is remembered that the unsaturation factor just discussed should increase compound formation in the antimony series beyond the normal extent.

If, now, we include in our comparison the three series of the type, HX:RX, studied in previous papers, we find compounds *intermediate in number and stability* between those of the aluminum and those of the antimony series. Now in the electromotive series of the metals, aluminum is *above* and antimony *below* hydrogen. Evidently, then, there is a *position*

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[31] The fact that divalent lead salts fall slightly out of line in previous work (ionization and solubility values in systems of the type, PbX_2:HX, being consistently a little too high) may be largely due to unsaturation. See, for example, Ref. 2c, p. 1490.

factor to be added to those already discussed, the tendency towards the formation of compounds in general decreasing as we go down the electrode-potential series. In the work on acid salts,[32] it was demonstrated that the rate at which compound formation decreases in stability as we approach hydrogen from either side, increases as the acid radical becomes weaker. A similar deduction may here be drawn, that the rate at which double salt formation decreases in stability, as we approach our reference radical from either side, increases as the electropositive character of this reference radical diminishes.

5. The Temperature Factor.—The manifest superiority of aluminum bromide systems over corresponding aluminum chloride systems in compound formation and solubility cannot justifiably be ascribed, however, to the relative positions of bromine and chlorine in the negative electrode-potential series. The main factor here is undoubtedly the temperature difference which exists between analogous curves. The melting point of aluminum chloride is almost 100° above that of aluminum bromide. In consequence, many of the compounds in the aluminum bromide series crystallize at temperatures far below the available experimental range for aluminum chloride mixtures, and the failure to isolate compounds in the latter series must frequently be due to the impossibility of securing sufficiently low temperatures for their separation as solid phases from the solutions containing them.

We have here illustrated, indeed, one of the fundamental limitations of the freezing-point curve method for determining the stability of addition compounds. The sharpness of the maximum on the freezing-point curve indicates the degree of dissociation of a compound into its components at its temperature of fusion only, and it is certain that the equilibrium point of the reaction $A + B \rightleftarrows AB$ will change, in most systems, very materially with the temperature. A compound very stable at its melting point may, in fact, be quite appreciably dissociated into its components at a temperature 100° higher.[33] We must, therefore, be cautious in drawing conclusions regarding the relative stability of compounds from freezing-point curves at very different temperatures, since under identical conditions their degrees of dissociation might very well be reversed. When the temperatures of fusion are not widely divergent, however, qualitative comparisons at any rate are certainly valid. If exact evidence is required, it can in many cases be obtained from the relative shift of the freezing-point curve of one of the components of the mixture from its ideal position, as has been discussed in detail in earlier articles.[34]

When we turn to consider *solubility relationships*, it is the temperature

[32] Ref. 3b, p. 1479.

[33] Iodine monochloride and 100% sulfuric acid are good examples.

[34] See, for example, Kendall and Booge, THIS JOURNAL, **38,** 1730 (1916).

of fusion of the *second component* which must be taken into account. This point has also been taken up in full in a previous paper,[35] to which reference should be made for a study of the conditions under which direct solubility comparisons between various systems are properly in order.

6. Internal Pressure Differences.—It has been demonstrated by Hildebrand[36] that, in non-polar systems, solubilities (or freezing-point depressions) are dependent primarily upon the relative values of the internal pressures of the two components. Where internal pressures are equal, the course of the curves may be calculated directly from the ideal-solution theory. As internal pressures diverge, solubility diminishes and when the divergence is very large, 2 liquid layer systems may result. The abnormality in the curves, due to this factor, is in the opposite direction from that induced by compound formation and may, in systems containing highly polar components, frequently be neglected.[37] In the present work, however, where the reference salts are all of very low polarity, it may be predicted that extreme internal pressure differences will exercise a very significant effect upon the character of the freezing-point diagrams.

The calculated values for the internal pressures of a number of the substances employed are given in Table III. These have been derived with

TABLE III

INTERNAL PRESSURES

Ref. subs.	$V_{20°}$	π (atm.)	Added bromide	$V_{20°}$	π (atm.)	Added chloride	$V_{20°}$	π (atm.)
$AlBr_3$	88.6	3,050	LiBr	25.1	35,600	LiCl	20.5	44,800
$AlCl_3$	54.7	4,120	NaBr	34.2	28,400	NaCl	26.9	37,100
$SbCl_3$	73.8	3,320	KBr	43.6	21,700	KCl	37.5	26,300
			AgBr	29.0	25,000	CuCl	28.0	27,100
			$ZnBr_2$	53.5	9,500	AgCl	25.7	28,200
			$CdBr_2$	52.4	10,700	HgCl	33.2	10,400
			HgBr	38.4	10,000[a]	$HgCl_2$	50.0	5,900
			$HgBr_2$	62.8	4,400[a]	TlCl	33.0	16,200
			CBr_4	97.3	2,300	$SnCl_4$	116.8	1,550
			$SnBr_2$	54.4	9,000			
			$SnBr_4$	131.0	1,770			
			$AsBr_3$	88.9	2,800			
			$SbBr_3$	86.8	3,250			
			$BiBr_3$	80.0	4,900			

[a] Value obtained by the method of van Laar, *J. chim. phys.*, **14**, 3 (1916).

the help of Hildebrand's equation:[38] $\pi = 20.65\ (5200 - 30\ T_b)\ V_{20°}$; where π is the internal pressure in atmospheres, T_b, on line the boiling point in degrees absolute, and $V_{20°}$ is the molecular volume at 20°. Strictly speaking, this last quantity should be referred to the substance in the liquid state, but

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[35] Ref. 2c, p. 1488.

[36] Hildebrand, THIS JOURNAL, **38**, 1452 (1916), and subsequent articles.

[37] See Ref. 2c, pp. 1483, 1498.

[38] Hildebrand, THIS JOURNAL, **41**, 1069 (1919).

in view of the notorious uncertainty attached to all internal-pressure data (the results throughout being merely relative, since different methods give values differing by as much as 1000 atmospheres in some cases) the substitution of the molecular volume in the crystalline state for substances melting above 20° does not affect significantly any of the conclusions drawn below.

The calcium salts and a number of other compounds of extremely low volatility are not listed in the above table, since the necessary data are not available. It is evident, however, from the equation that the internal pressures of all such compounds must be very high, greater than 12,000 atmospheres.

When we study the results of the present investigation in connection with Table III, we find that the systems fall into three main classes. In the first, the internal pressures of the 2 components are not markedly divergent, the second component resembling the reference salt in being only very slightly polar. Unless modified by compound formation (as in the system, $AlBr_3$–$SbBr_3$) the solubility curves in systems of this type are essentially ideal; no tendency towards incomplete miscibility in the liquid state is ever apparent.

In the second class of systems, internal pressures are very widely divergent, the second component being a highly polar salt. In such cases, limited miscibility in the liquid state is almost invariably a distinguishing feature of the freezing-point diagram. That the 2 liquid layer region extends over only a comparatively short composition interval in the majority of these systems is undoubtedly due to the opposing effect exerted by extensive compound formation between the 2 components. The addition compounds formed may be predicted, in general, to resemble their more polar constituent in nature, being readily broken up into ions.[2b] Presumably, in common with other ionically unstable substances, they will possess high internal pressures, and should consequently be perfectly miscible in the liquid state with each other and with the more polar salt. Partial miscibility should be restricted, therefore, to that portion of the system in which the slightly polar reference salt is in large excess. Reference to the diagrams will show that this is in point of fact the case.

The third class of systems falls intermediately between those already discussed. The second component here is a "transition" salt with an internal pressure decidedly but not overwhelmingly above that of the reference substance. We should here expect to obtain freezing-point diagrams in which the abnormal course of the curves indicates a strong tendency towards partial miscibility in the liquid state, without the actual appearance of a stable 2 liquid layer region. Some rather remarkable examples of this nature have indeed been obtained. The system, $AlBr_3$–$CdBr_2$, (see Fig. 3, Curve B) may be cited. In this system the freezing-point curve for the compound $2AlBr_3.CdBr_2$ exhibits most pronounced changes in slope. A rise of 94° between 0.7 and 4.5 mole percentage cadmium bromide is followed by a rise of only 7° between 4.5 and 12.5 mole percentage, then by a rise of 13° between 19 and 26 mole percentage. The almost horizontal central section of the curve is, as has been discussed by Roozeboom,[39] a characteristic of systems in which the boundary curve of a metastable 2 liquid layer region just fails to intersect the freezing-point curve. While in the system, $AlBr_3$–$CdBr_2$, partial miscibility could not be established by supercooling, owing to the ready separation of the stable solid phase, the validity of the explanation just advanced for the inflexion point in the curve is beautifully confirmed in another system of the same character, namely the system, $SbCl_3$–$SnCl_4$. Here the internal pressure of the second component is decidedly *less* than that of the reference salt, and the experimental data (see Fig. 6, Curve A) show a freezing-point curve with an exceptionally flat central portion, and a 2 liquid layer region lying immediately beneath. The temperature drop in the freezing-point curve for antimony trichloride in this system is only 0.6° between 24 and 61% of stannic chloride,[40] and the boundary curve of partial miscibility comes within 0.2° of escaping from the metastable area.

The only noteworthy exceptions to the above classification are systems containing salts of lithium as second component. As may be seen from Table III, lithium chloride and bromide possess the highest internal pressures of all the salts listed in their respective columns, yet each is perfectly miscible in the liquid state with the corresponding aluminum salt. A logical explanation of this apparent discrepancy is available, however, in the superior complexity of the compounds existent in these lithium systems. In the case of the bromide, a compound of the composition $7AlBr_3.LiBr$ is actually isolable. A substance containing such a preponderant proportion of the slightly polar component can scarcely be expected to show an internal pressure so very markedly divergent from that of aluminum bromide as in the case of the other systems shown in Fig. 1, and while the abnormal change in the slope of its freezing-point curve in the neighborhood of the aluminum bromide composition axis indicates that a tendency towards immiscibility in the liquid state exists, this tendency is not sufficiently pronounced to induce the formation of 2 stable liquid layers.

In the case of the system, $AlCl_3$–$LiCl$, the existence of double salts containing high percentages of aluminum chloride is masked by the high tem-

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[39] Ref. 20, p. 133.

[40] If the average molecular heat of solution for antimony trichloride throughout this region is calculated from the freezing-point depression equation [see Ref. 20, **1**, 274 (1904)], the stupendous value of 250,000 calories is obtained. The normal molecular heat of solution for antimony trichloride [Tolloczko and Meyer, *Chem. Zentr.*, **1910**, II, 1024] is only 3010 calories. It has recently been noted by Sidgwick and Taylor [*J. Chem. Soc.*, **121**, 1856 (1922)] that an unexpectedly high value denotes that the system must be approaching the temperature at which 2 liquid layers separate, but no figure of this magnitude has previously been recorded.

perature range of the freezing-point curve, but the exceedingly flat character of this curve (see Fig. 5, Curve D) is indicative of the presence of such complexes in solution, their internal pressures being evidently just not sufficiently divergent from that of aluminum chloride to necessitate partial miscibility in the system.

7. Molecular and Atomic Volumes.—Inequalities in the molecular volumes of the two components of a liquid mixture have also been cited as a factor in bringing about immiscibility. Reference should be made, in particular, to the work of Holmes,[41] from which it has been concluded that when the ratio of the molecular radii exceeds 1.618 to 1 partial miscibility will occur, while a ratio higher than 2.414 to 1 will induce complete immiscibility. Whatever validity these rules may possess in other fields, they are certainly inadequate throughout the present investigation, as may be seen from the data in Table III. In none of the mixtures studied does the molecular-volume ratio of the components exceed the lower limiting value of $(1.618)^3:1$, yet partial miscibility is very frequent.

In fused-salt systems, indeed, where the polarity of at least one component is generally marked, it appears more logical to consider atomic (or ionic) volumes as the factors which directly affect compound formation and solubility. Let us take, for example, a highly polar salt of the type RX. If this forms with a second less polar substance AB an equimolecular compound RX.AB, two possibilities exist with regard to the constitution of this complex.[42] Either the neutral molecule AB will be combined with the positive radical R, in which case the ionization of the complex will be represented by the equation: $\mathrm{RX.AB} \rightleftarrows (\mathrm{R.AB})^+ + \mathrm{X}^-$, or it will be attached to the negative radical X, and dissociation will give the ions R^+ and $(\mathrm{X.AB})^-$.

What will happen if we vary the atomic volume of the positive radical R in each instance? In the first case, if we restrict our comparisons to radicals of the same valence, then we may predict that those with smaller volumes, owing to the greater attractive forces existing at their surface,[43] will give addition compounds with neutral molecules more readily than those with larger volumes, where the forces at the surface are relatively weak. This prediction is in accordance with experimental facts. Thus lithium has the smallest atomic volume of the alkali metals, and lithium ion is more highly hydrated in aqueous solution than sodium or potassium ions. Similarly, magnesium ion is more highly hydrated than calcium, strontium or barium.

If, on the other hand, addition of the neutral molecule is confined to the

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[41] Holmes, *J. Chem. Soc.*, **103,** 2147 (1913).

[42] This topic is developed in greater detail in an article by Kendall and Haring soon to appear in *Proc. Nat. Acad. Sci.*

[43] See Thomson, *Phil. Mag.*, [6] **27,** 776 (1914).

negative radical X, the stability of the complex will depend upon the residual affinity of this radical. The smaller the volume of the radical R, the greater will be the attractive forces exerted by it upon X, and the less freedom will X have to engage itself with other molecules. We should, therefore, expect compound formation in this case to *increase* as the atomic volume of R is increased.

The volume factor in the case of the radicals X, A and B may be similarly analyzed. Inasmuch, however, as the conclusions arrived at depend, as above, upon the mode of ionization of the double salt, the application of the atomic volume factor to the results of this investigation will be profitably postponed until conductivity determinations are presented.

8. The Atomic Number Factor.—Abegg[44] has noted that addition compound formation, within a given group of the periodic system, increases with increasing atomic weight. In the present work a good example of this factor (which may now more logically be referred to atomic number) is offered in Systems 18–21 of the aluminum bromide series, where the tribromides of phosphorus, arsenic, antimony and bismuth, respectively, are the second components. The first 2 systems give no isolable compounds. In the case of antimony tribromide, the freezing-point curve indicates an equimolecular compound, very highly dissociated into its components on fusion. With bismuth tribromide, finally, a much more stable complex is isolated (see Fig. 4, Curves C, D and E).

Another illustration is available in the antimony trichloride series, where lithium and sodium chlorides are insoluble while potassium chloride gives two isolable compounds. In general, however, the influence of other factors in systems containing a highly polar component is sufficient to mask this effect entirely.

9. The Association Factor.—A detailed examination of phenol-cresol mixtures[45] has shown that, in systems consisting of two similar components, both associated, compound formation may occur by substitution instead of by addition, and the physico-chemical characteristics distinguishing substitution from addition compounds have been carefully noted. When both components are highly polar, disintegration and recombination of the various molecular and ionic types present will evidently result, finally, in an almost haphazard replacement of the different radicals by one another at all points of the original associated molecules.[46] If the attractive forces

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[44] Abegg, *Z. anorg. Chem.*, **39,** 361 (1904).

[45] Kendall and Beaver, This Journal, **43,** 1853 (1921).

[46] For a justification of the term "associated" as applied to highly polar substances such as fused salts, see Ref. 2b, p. 1419. The following comment of Milner [*Trans. Faraday Soc.*, **15,** 150 (1919)] is also instructive: "The use of the words 'completely dissociated' is perhaps rather misleading in this connection...... the state might equally well be described as one of partial association, controlled not by chemical interionic forces but solely by electrical ones."

between the constitutent groups are such that a certain substitution complex is exceptionally stable, then we may expect to isolate this complex under suitable conditions of temperature and composition. If the original components constitute the most stable aggregates, then the freezing-point curve will presumably show a simple eutectic. If no particular arrangement predominates in stability, the system will tend to yield "mixed crystals" on solidification.

In fused-salt mixtures previously studied, two similar highly polar components have usually been selected, and all of the 3 types of curves mentioned above are to be found in the literature.[47] The chlorides of the alkali metals all yield either eutectics or solid solutions. The systems, lithium sulfate-potassium sulfate, and sodium hydroxide-rubidium hydroxide, however, furnish stable compounds. Conspicuous examples of the same type in other fields are the system, sodium-potassium, (with the compound of the formula NaK)[48] and the system, iodine-chlorine, (with the compounds iodine monochloride and iodine trichloride).

It is of course impossible, in systems of this type, to derive any general rules regarding compound formation from a study of the freezing-point diagrams. In the present work, therefore, an attempt has been made to obviate the confusion that would undoubtedly arise from the appearance of substitution compounds in the curves by selecting as reference salts, in all 3 series, substances which are only slightly polar and consequently not very highly associated. The fact, already remarked upon in an earlier section, that not a single instance of solid solutions has been met in the course of the whole investigation is very reassuring evidence that the disturbing influence of substitution compound formation has thus been reduced to a minimum throughout. How greatly the examination of the effect of the various other factors has thereby been facilitated can be judged only by endeavoring to derive generalizations of any value from the results of previous workers.[6]

Final Review.—It is unfortunate that more of the factors which have been discussed in the preceding sections cannot be, in succession, dropped out of consideration, so that strictly comparative data with respect to each single factor in its turn might be obtained. However, it is impossible in general to vary any one factor without varying several others very significantly, and the opposing effects so introduced often render the interpretation of single systems somewhat uncertain. The examples cited in

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[47] For representative diagrams reference should be made to Landolt-Börnstein, Ref. 26.

[48] It is important to note that Kraus [THIS JOURNAL, **44,** 1216 (1922)] has also concluded, from an examination of physico-chemical properties, that this compound of highly electropositive elements is fundamentally different in character from compounds formed by two dissimilar metals, which are to be regarded as addition compounds or "salts."

each section, nevertheless, suffice to indicate, at least qualitatively, the influence exerted by each factor upon compound formation and solubility. The reader will be able to discover for himself many additional confirmatory illustrations by analysis of the freezing-point data for each system and of the annexed diagrams. Naturally, some minor inconsistencies exist, but these are remarkably few in view of the multiplicity of assisting and opposing factors which come into play at every point. The general agreement is all that can be expected.

The theoretical basis for the effect of each factor upon compound formation and solubility can be outlined only in a preliminary manner here. As will be seen below, it is evident even from the present work that certain of the influences are very intimately interlocked, and it is probable that as we advance in our understanding of the field, a common fundamental origin of all the factors will become apparent.

The *diversity* factor, which is undoubtedly the most important of all, must be regarded as the "driving-force" behind any combination which takes place between the two components on admixture. The formation of complexes is thus conditioned primarily by the differences in character (that is, in the positive or negative nature) of the several groups concerned. This point has been discussed in detail in previous articles.[49] The use of the normal potentials of the elements in the electromotive series as a basic standard for diversity is, however, not strictly defensible.[50] In the first place, these potentials are referred to aqueous solutions, in the majority of which the ions are very extensively hydrated. Now, only the non-hydrated fraction of the ions can establish a potential difference against the electrode,[51] and this non-hydrated fraction will certainly differ greatly with different ions, so that however dilute the solution, electromotive-force measurements can never give affinity values which are fundamentally comparable for a series of radicals. When we consider moderately concentrated solutions, the change in water concentration necessarily involves a variation in ionic hydration, and in this region electromotive-force measurements no longer afford a logical basis for calculating ionic activities, since the proportion of non-hydrated to total ions is changing with the concentration of the solution. This is a point which is almost invariably neglected in comparing electromotive-force "activity coefficients" with conductance ratios Λ_v/Λ_∞, and is presumably responsible in large measure for the very significant differences obtained.[52]

When we consider elements of different *valence*, the employment of normal potentials appears even more arbitrary. There is no more reason

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[49] See particularly Ref. 2b.

[50] Compare Ref. 2c, p. 1501.

[51] Kendall, *Proc. Nat. Acad. Sci.*, 7, 60 (1921). See also Bjerrum, *Z. anorg. Chem.*, 109, 275 (1920).

[52] See, for example, Noyes and MacInnes, THIS JOURNAL, 42, 243 (1920).

(except that of convenience) for choosing normal concentrations as standard than, say, one-millionth normal, and since the change in electrode potential with concentration varies with the valence of the ion, the spacing of univalent, divalent and polyvalent ions in the series would, on the latter basis, be very materially altered. For the present, nevertheless, in default of sufficient exact free-energy data for establishing true electro-affinities, we must make shift with the series as it stands. The results obtained amply justify this procedure, and would seem indeed to indicate that the relative allocations of most of the radicals must be substantially accurate.

Further examination of the valence factor is deferred to a subsequent article. The *unsaturation* factor scarcely needs discussion; it is only to be expected that a radical with unsatisfied valences will exhibit an abnormal trend towards addition compound formation. The *position* factor, however, merits somewhat closer analysis.

As we go down the electrode-potential series of the metals, we find that the halogen salts become less and less stable. The heats of formation of the alkali halides are all very high, and these salts consequently show no tendency to decompose. At the foot of the series, however, we have the halides of the noble metals, which break up very readily, as by exposure to light or gentle heat. Now, the addition compounds which one halide forms with other halides will, in general, be more unstable than the simple salts themselves, in view of the greater complexity of the molecule. It is consequently highly improbable that the halide of a metal low down in the electrode-potential series will be capable of forming many *directly isolable* double salts with other halides, however great the diversity factor. The existence of such compounds may in many cases be readily established under suitable conditions, such as in aqueous solution at low temperatures, but at the higher temperatures of the fused salt mixtures they are practically completely dissociated into their components. This accounts for the paucity of isolable compounds in the antimony trichloride series (see Table II).

The *temperature* factor has already been adequately discussed. For a detailed examination of the *internal-pressure* factor, reference should be made to the valuable articles of Hildebrand. A partial analysis of the *atomic-volume* factor has been given in an earlier section. It remains to be noted here that ultimately the diversity factor itself must be correlated with this question of atomic volume, since the electrode potential of any element against a standard concentration of its ions will be fundamentally dependent upon the "structure" of the atom (that is, the nature and magnitude of the forces existent between the nucleus and the exterior electrons), and will therefore be a function of the atomic volume. Our knowledge of the inner fabric of the atom is far too fragmentary at present to allow us to establish any quantitative connection between the two factors, but it is both interesting and important to recognize the general rule that, elements with very large atomic volumes are either highly electropositive or highly electronegative, while those with very small atomic volumes are grouped in lower positions in their respective series.

It is a debatable point, finally, whether the *atomic-number* factor is distinct from that of atomic volume. The atomic volumes of the elements in most groups of the periodic table increase regularly with increasing atomic number, and the greater stability of addition compounds as we go upwards through any given group may consequently be due to this variation. We shall return to this and to other aspects of the problem in future communications.

Summary

The freezing-point curves of more than 50 binary fused-salt mixtures have been investigated, and 49 new addition compounds have been established. The experimental work falls into 3 series: (*a*) aluminum bromide with other bromides, (*b*) aluminum chloride with other chlorides, and (*c*) antimony trichloride with other chlorides.

The factors affecting compound formation and solubility in these 3 series have been critically examined. As in previous work, the diversity of the constituent radicals of the component substances has been found to be the main influence. Other factors that have been discussed are valence, unsaturation, position in the electrode-potential series, temperature, internal pressure, atomic volume, atomic number and association.

The analysis of the freezing-point curves obtained, in view of the simultaneous operation of all these factors, is rather involved in most cases. Since a *brief* summary of the conclusions drawn cannot readily be presented, the reader is referred to the final review of results on the preceding pages.

Two very unusual types of curve have been encountered, of which Systems 2 (Fig. 1, Curve E) and 53 (Fig. 6, Curve A) are good examples. In the former, a compound breaks up into two partially miscible liquid layers when heated, and its true melting point cannot be determined. In the latter, an exceedingly small change in the temperature of fusion over a wide composition range is induced by the existence of a 2 liquid layer region just below the freezing-point curve.

The discussion will be continued in a subsequent communication, in which conductivity data will be presented.

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