critical point in the presence of 0.0025 N succinic acid is identical with that in pure water, thus indicating the removal of the succinic acid from solution as a molecular complex.

A comparison of the effects of tartaric acid and sodium tartrate (Fig. 11) is of interest since precipitation is encountered with as low as 0.0025 N sodium tartrate whereas 0.02 N tartaric acid increases the critical concentration. Such an increase is easily explainable on the basis of complex formation.

A study of Fig. 12 shows that sulfuric acid brings about precipitation at approximately the same concentration as sodium sulfate. This indicates that, under the experimental conditions employed, complex formation between the components does not occur.

Studies of the electrical conductivity of dodecylammonium chloride in water-organic solvent systems[9] show that the addition of a solvent such as methanol or ethanol to aqueous solutions of this colloidal electrolyte greatly increases the concentration at the critical point. This effect is the opposite of that produced by the addition of salts and should be nullified by such additions. Figure 1 shows the electrical conductivity of dodecylammonium chloride in 25 vol. per cent. aqueous methanol, and in 0.02 N sodium chloride in 25 vol. per cent. aqueous methanol as well as in sodium chloride solutions. The critical concentration in the sodium chloride-methanol system is approximately the average of those of the methanol solution and the 0.02 N sodium chloride solution, thus indicating that the effects of sodium chloride and methanol are mutually compensating.

Summary

The conductivity by difference of dodecylammonium chloride has been determined in the presence of a number of salts and acids.

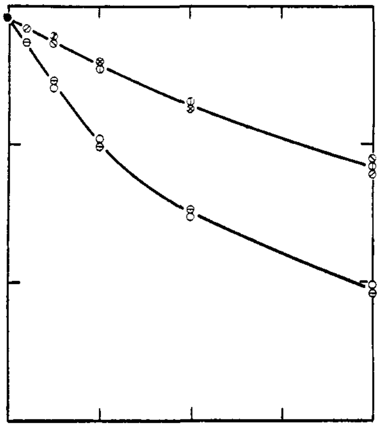

Fig. 13.—Critical concentration of dodecylammonium chloride in presence of chlorides and nitrates at 30°: O, HNO_3; ⊖, $NaNO_3$; ⦶, HCl; ⦸, $BaCl_2$; ⌀, NaCl.

Salts and strong acids reduce both the equivalent conductivity and the critical concentration. The reduction of the critical concentration in the presence of such electrolytes is independent of the nature and concentration of the cation of the added electrolyte. Weak acids, on the other hand, form molecular complexes with dodecylammonium salts and their presence does not reduce the critical concentration.

The addition of sodium succinate, sodium tartrate or sodium sulfate brings about precipitation in dilute aqueous solutions of dodecylammonium chloride. This effect is not encountered with weak acids owing to molecular-complex formation.

The increase in the critical concentration of dodecylammonium chloride brought about by the addition of methanol is nullified by the addition of sodium chloride.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 10, 1948

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[9] Ralston and Eggenberger, *J. Phys. and Colloid Chem.*, **52**, 1494 (1948).

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

Metal-Salt Interactions at High Temperatures: The Solubilities of Some Alkaline Earth Metals in their Halides[1]

BY D. D. CUBICCIOTTI[2] AND C. D. THURMOND

It has long been known that certain metals may be dispersed in their molten salts.[3] The phases thus formed, when chilled to room temperature, are salt-like, intensely colored, good reducing agents (of the order of the metal dispersed in them) and may have globules of metal embedded in them. This phenomenon was attributed to the reduction of the salt by the metal at high temperature with the formation of a lower valent salt (unstable with respect to the metal and normal salt at room temperature). Later work, due mainly to R. Lorenz,[4] attempted to show that the metal was being colloidally dispersed throughout the salt. In the case of bismuth and

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[1] This research was directed by the late Prof. E. D. Eastman and carried on for the Manhattan Project.

[2] Present address: Department of Chemistry, Illinois Institute of Technology, Chicago, Ill.

[3] Davy, *Trans. Roy. Soc.* (*London*), **97**, 1 (1807); Bunsen and Kirchhoff, *Pogg. Ann.*, **113**, 364 (1861); Stockem, *Z. angew. Chem.*, **17**, 341 (1904); Guntz and Benoit, *Bull. soc. chim.*, [4] **35**, 709 (1924).

[4] Lorenz and Eitel, "Pyrosole," Leipzig, 1926.

cadmium systems, a study of the liquid–solid phase equilibria indicated that the metal dissolved in the salt with a depression of the freezing point and hence was not colloidally dispersed.[5]

The heavier alkaline earth elements are among those that exhibit this phenomenon. Probably due to experimental difficulties, only few quantitative data have been reported for them.[6] Since these data indicated that large amounts of alkaline earth metals may be dispersed in their halides, these systems were chosen for the present investigation.

Experimental

Methods.—Two distinct methods were used to obtain the data. The freezing points and condensed three-phase halts were determined by measuring the rate of cooling of a sample of known over-all composition. The limits of liquid–liquid miscibility were determined by chemical analysis of the phases resulting from an equilibration of a mixture at a fixed high temperature followed by quenching to room temperature.

To measure the rate of cooling of a sample, about 30 g. of it was melted into an "Armco" iron crucible (7/8" × 2") contained in a long porcelain test-tube (18" × 1"). The porcelain tube was fitted with a rubber stopper sealed on with wax with inlet tubes such that the tube could be evacuated and filled with purified helium. An "Armco" iron thermocouple well (wall thickness about 0.01") was held in the melt so that the thermocouple junction would be in the center of the melt. The system was heated in a tubular electric resistance furnace to a temperature at least 50° above the m. p. of the highest melting component of the sample for thirty minutes or more and then allowed to cool slowly.

The temperature of the cooling sample was measured every thirty seconds with a platinum-10% rhodium thermocouple (cold junction in an ice-bath) calibrated by the Bureau of Standards, a Leeds and Northrup "Portable Precision Potentiometer" being used to measure the potential to 5 microvolts. At least two cooling curves that showed the same kinds of temperature halts to ±1° were obtained for each sample. The typical cooling curve for the pure components with this arrangement showed a constant temperature for a liquid–solid transition lasting for from three to ten minutes.

To determine the limits of the miscibility gaps a sample of about 10 to 20 g. (of composition such as to give a final mixture of half-metal and half-salt phases) was melted into an iron crucible fitted with an iron cap. This crucible was tied to an iron thermocouple well and sealed into a long porcelain test-tube which was then evacuated and filled with purified helium. The system was heated to the desired temperature in an electric resistance furnace whose temperature was maintained constant to ±10° with a "Wheelco Potentiotrol." The sample was equilibrated for two to three hours and then was quenched by removing the iron crucible from the porcelain container and dipping the lower half of the crucible in water. The crucible was then cut into transverse sections and samples of the metal rich and salt rich phases taken for analysis. The weight of sample and total amount of halide ion were determined, and from these the per cent. of metal in the salt-phase and salt in metal-phase were calculated.

Materials.—The metals used throughout were of the purest the authors could obtain commercially. Table I gives the observed freezing points of these metals as compared to literature values. The freezing point data as given by van Arkel[7] are scattered; however, the values quoted for the purest, or most highly distilled, metal are included in Table I. Strontium is known to exist in two crystalline modifications[7]; however, no transition temperature appears to be reported in the literature. The present authors find a halt in the cooling curve of the metal at 589° which they attribute to this transition.

TABLE I

THE FREEZING POINTS OF METALS USED COMPARED TO LITERATURE VALUES

Metal	Observed freezing point, °C.	Literature freezing point,[7] °C.
Ca	828	849
Sr	770	771
Ba	717	710

The salts were prepared by dehydrating reagent grade hydrated material. The chlorides and bromides were dehydrated by gradually raising the temperature of the samples under a high vacuum (10^{-4} to 10^{-6} mm. of mercury) over a period of several days up to 400 to 500°. This procedure was sufficient to produce dry salts which, on solution, showed neutral reactions to phenolphthalein and hence little or no oxide formed during dehydration. Strontium iodide hexahydrate was dehydrated by slowly warming it with an equimolar quantity of ammonium iodide under high vacuum to 400°. The ammonium iodide served to supply an atmosphere of hydrogen iodide gas which repressed the formation of strontium oxide. The ammonium iodide sublimed off during the process leaving the dehydrated salt behind. This procedure gave an anhydrous salt containing less than 0.1 mole per cent. strontium oxide.

The metals and anhydrous salts were handled only in a moisture-free atmosphere of nitrogen or carbon dioxide.

Results

Several alkaline earth metal–metal halide systems were investigated by these methods. The data obtained are presented in Figs. 1 to 5. The methods employed are only capable of detecting the liquidus curves and condensed three-phase halts; thus the curves drawn are liquidus curves only. In some of the systems there is definite evidence of solid solution, *i. e.*, from the lowering of the solid phase transition temperatures when small amounts of foreign substance are added to the pure component. Since the solid solution regions were not quantitatively investigated in this work, no indications of the limits of solid solution or of the solidus curves are drawn into the diagrams. This is not intended to imply their absence.

In all these systems the metal phase was found to have the same appearance as the pure metal used. However, the salt-rich phase was highly colored in each case, the intensity of color depending on the percentage of metal dissolved. The salt-rich phases evolved hydrogen gas from water even more vigorously than the bulk pure metals and were rapidly oxidized in moist air to white powders. In every system the metal was found to float on the salt-rich phase.

In determining the freezing points of the calcium–calcium chloride system the eutectic was found to have a tendency to cool below the eutectic temperature and then freeze with a sudden rise in temperature. To overcome this difficulty in the salt-rich region the melt was seeded with

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(5) Aten, *Z. physik. Chem.*, **66**, 641 (1909); **73**, 578 (1910).

(6) Guntz, *Chimie et Industrie*, Numero special, Feb., 1929, p. 458.

(7) Van Arkel, "Reine Metalle," J. Springer, Berlin, 1939, pp. 132-138.

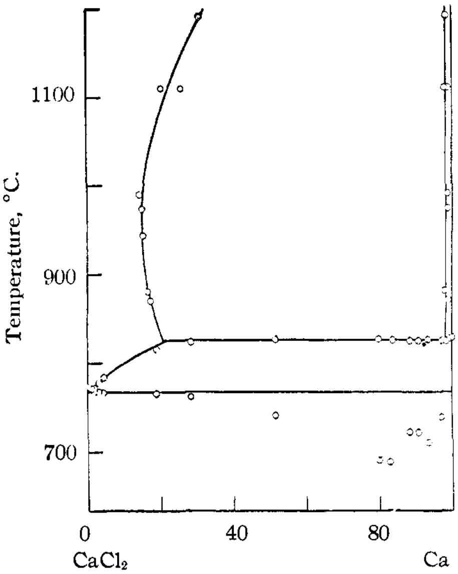

Fig. 1.—The system calcium-calcium chloride.

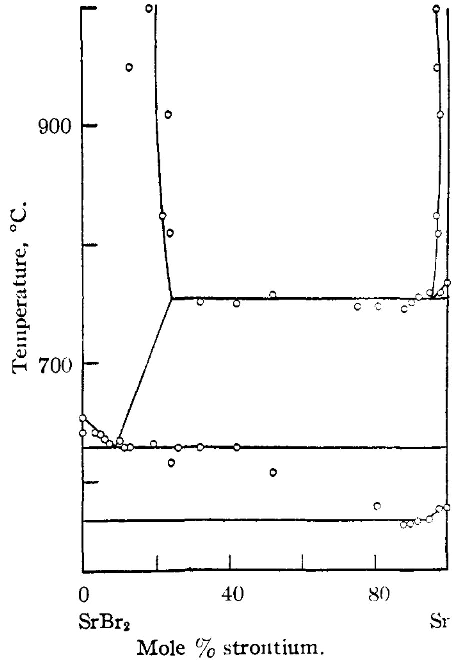

Fig. 2.—The system strontium-strontium bromide.

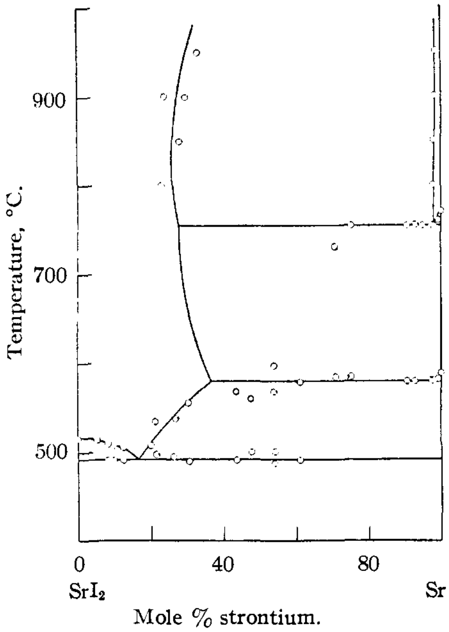

Fig. 3.—The system strontium-strontium iodide.

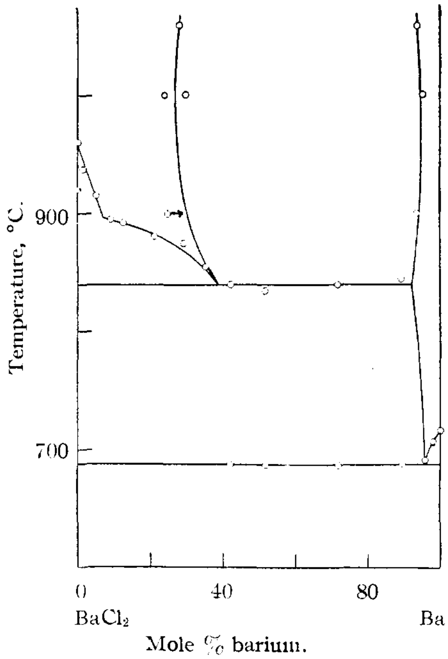

Fig. 4.—The system barium-barium chloride.

crystals of pure calcium chloride just at the expected eutectic temperature (767°). This procedure had no effect when there was more than 20 mole % metal because a layer of frozen metal over the liquid rendered the latter inaccessible to seeds. For this reason the eutectic temperature halts in the metal-rich region (80% calcium and greater) are badly lowered.

In the strontium systems a halt was observed for pure metal at 589°. The temperature of this halt was lowered a total of 9° by the addition of salt. The halt appeared in the cooling curves of the metal as only a small effect and became even smaller as salt was added; thus only a few points, near the metal end, are plotted for this effect in Fig. 2, and in Fig. 3 the points are scattered.

In Figs. 6 and 7 are given cooling curves for the metal rich region of the strontium–strontium iodide system and the calcium–calcium chloride system, respectively. They serve to show the type of data from which were evolved the phase

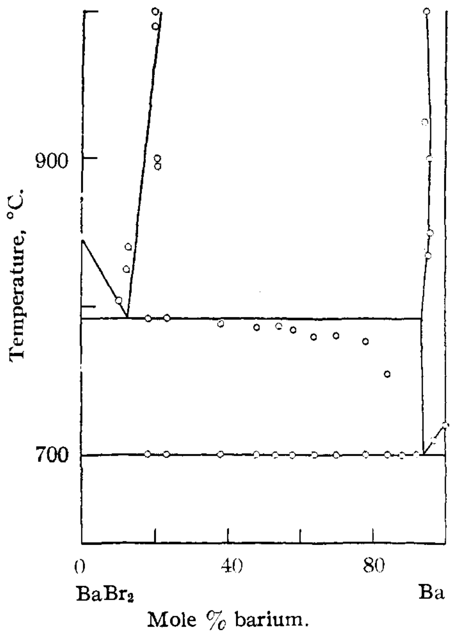

Fig. 5.—The system barium-barium bromide.

diagrams and also the differences which allowed the authors to assign a second break in the metal-rich curves of the calcium system to supercooled eutectic halt and those of the strontium systems to a transition in the metal. The upper break in each curve represents the solid–liquid equilibrium for the metal. The lower breaks in the curves of Fig. 6 were taken as due to a transition in the metal since the break was sharp in the pure metal but less distinct when salt had been added. The curves of Fig. 7, for the calcium system, illustrate a case in which no transition was observed for the pure metal, but a heat effect appeared as salt was added. This second break was interpreted to be the badly supercooled eutectic halt of the system not only because the break did not appear in the pure metal but also because it had the typical looped shape of a supercooled halt.

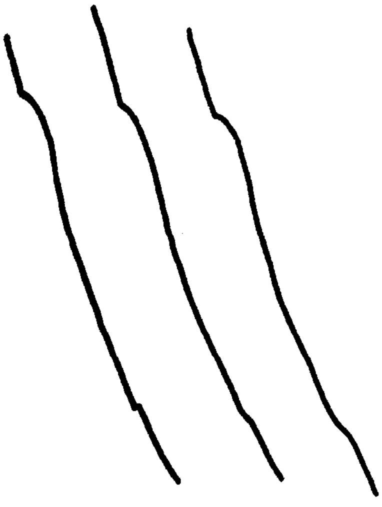

Fig. 6.—The cooling curves of pure strontium, strontium with 1 mole % strontium iodide, and strontium with 2 mole % strontium iodide.

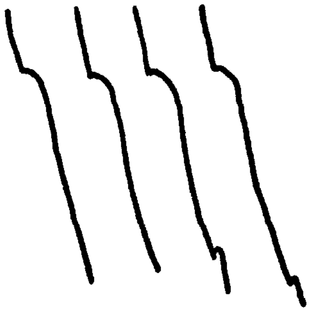

Fig. 7.—The cooling curves of pure calcium, calcium with 0.5 mole % calcium chloride, calcium with 3 mole % calcium chloride, and calcium with 7 mole % calcium chloride.

In pure barium chloride a transition occurred at 920°. From the break in the liquidus curve in the salt-rich region it would appear that the transition temperature is lowered by the addition of metal. Since no breaks corresponding to the transition were observed for salt containing some metal, no curve is drawn in that region of Fig. 4.

In Table II are given the solubilities of the metals of the second group of the periodic table in their molten chlorides. For the main group and the sub-group considered separately, the solubility of the metal increases with the atomic weight. For the whole group this is only roughly the case.

Table II

The Solubilities of the Metals of Group II in their Molten Chlorides

Metal	Soly. in chloride, mole %	Temp., °C.	Rad. of +2 ion Å.[8]	$-\Delta F_{298}$, kcal./mole of formation salt[9]
Mg	1.2[a]	900	0.65	141.2
Ca	16[b]	900	0.99	180.1
Sr	~20[c]	900	1.13	186.0
Ba	30[d]	900	1.35	193.2
Zn	10^{-4}[e]	500	0.74	88.5
Cd	16[f]	650	0.97	82.7

[a] Shurin, *Metallurg.*, **10**, No. 4, 87 (1935). [b] From Fig. 1. [c] Estimated from Figs. 2 and 3. [d] From Fig. 4. [e] Von Hevesy and Lowenstein, *Z. anorg. Chem.*, **187**, 266 (1930). [f] Aten, *Z. physik. Chem.*, **73**, 578 (1910).

Also in Table II are given the radii of the +2 metal ions and the standard free energy of formation of the chloride of the divalent metal at 298°K. The solubility of the metal is seen to increase as the size of the cation. Mercury is omitted from the table for lack of data on its solubility in its chloride. The free energy of formation of the salt

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(8) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y.

(9) Brewer, Bromley, Gilles and Lofgren, "The Thermodynamic Properties of the Halides," declassified report, Manhattan Proj., Metallurgical Project Reports.

seems to bear no relation to the solubility of the metal, considering the group as a whole. That is, the reducing strength of the metal in going to the dichloride is not the major factor in determining its solubility in its dichloride.

It is not possible from the phase diagrams alone to decide on the nature of the solutions of metals and salts; however, the data do show that the mixtures are true solutions because the melting points of the pure substances are lowered by the admixture of the conjugate component. It is further of interest to note the relatively high solubility of salt in metal. This phenomenon must then be considered in the production of pure metals from their halides.

The authors are indebted to Dr. Leo Brewer for valuable suggestions and comments.

Summary

The temperature–composition diagrams for the systems: calcium–calcium chloride, strontium–strontium bromide, strontium–strontium iodide, barium–barium chloride, and barium–barium bromide were determined in the range of about 500 to 1000°. The diagrams are remarkably similar in form. The two liquid components are mutually soluble to a limited extent—the mutual solubility being roughly greater the greater the cation radius.

BERKELEY, CALIF. RECEIVED AUGUST 19, 1948

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Imaginary Contact Angles and the Jones–Ray Effect

BY ALBERT SPRAGUE COOLIDGE

When the surface of a liquid forms a concave meniscus in a cylindrical tube or between parallel plates, it is usually stated that it must either be tangent to the walls[1] (perfect wetting) or meet them at an angle of contact α, accordingly as the free energy of the solid–vapor interface is equal to or less than the sum of those of the solid–liquid and liquid–vapor interfaces. Let these energies be denoted by s', s, and σ, respectively, in the case of the first two adopting Gibbs's[2] definition [676] which ignores the unknown but constant energy of the material of the tube or plates. Then

$$\cos \alpha = (s' - s)/\sigma \qquad (1)$$

This gives real values to α only if $s' \leqslant s + \sigma$. The possibility that $s' > s + \sigma$ appears to be excluded by the imaginary contact angle, which can be interpreted as meaning that the meniscus and the wall would nowhere be in contact, and also by energetic considerations, which suggest that the solid–vapor interface would be completely invaded by a thick layer of liquid. Now, Langmuir[3] has recently proposed an explanation of the Jones–Ray effect based precisely on the theory that in dilute electrolytic solutions the meniscus in a capillary rise tube has a sensibly smaller radius than that of the tube itself, because of the presence above it of a wetting film which reduces by its own thickness the effective radius of the tube. According to the strict thermodynamic analysis of Gibbs, however, such a film is merely adsorbed at the solid–vapor surface, and does not constitute a separate bulk phase with a determinable thickness. Hence it is legitimate to say that in the Langmuir model the meniscus and wall do not meet and there is an imaginary contact angle. It is the purpose of this investigation to show that such an imaginary angle of contact is in harmony with mechanical and thermodynamical requirements, but that Langmuir's method of calculating the resulting correction to the apparent surface tension of a liquid is incorrect.

As a simple basis for discussion let us take a system in which all phase boundaries are normal to a common plane, which they intersect in one of the patterns shown in Fig. 1. The heavy lines represent a pair of parallel plane walls, and the circular arcs show the cylindrical portions (hereafter called menisci) of free surfaces separating masses of an involatile liquid from effectively empty space. We shall presently see that these free surfaces must be expected to depart from their cylindrical figure in the immediate neighborhood of the walls, as indicated qualitatively in the right-hand halves of the figures. The left-hand halves are drawn differently in order to show the geometrical relations, but do not imply any asymmetry in the actual systems. We shall ignore gravity, making the orientation immaterial, but for definiteness in future references we shall picture the walls and the common normal plane (the paper) as vertical. In each of the six cases shown, let R be the radius of the meniscus, reckoned positive for a concave surface, and let Δ be the distance from one wall to the nearest vertical plane which can be drawn tangent to the complete cylinder of which the meniscus forms a part, reckoned positive if this plane lies between the walls. Furthermore, let α be a parameter, called the contact angle, and defined as the number whose cosine is equal to $1 + \Delta/R$ in cases (a), (b) and (c), or to $-1 + \Delta/R$ in cases (d), (e) and (f). In the first and last cases α

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[1] In this paper the word "wall" will be used for brevity to indicate the inside surface of the tube or plate.

[2] All references to Gibbs are from "The Collected Works of J. Willard Gibbs," Vol. I, Longmans, Green and Co., New York, N. Y., 1928. Equation numbers in [ ] are from the paper "On the Equilibrium of Heterogeneous Substances."

[3] I. Langmuir, *J. Chem. Phys.*, **6**, 873 (1938).