Fig. 4.—Polarogram of nitrobenzenesulfonamide: 0.001 M solution in 0.1 N NaOH.

Fig. 5.—Polarogram of nitrobenzenesulfonamide: 0.001 M solution in 0.113 N HCl.

Summary

1. p-Hydroxylaminobenzenesulfonamide, p,p'-azoxybenzenesulfonamide, and p-nitrobenzenesulfonamide were examined polarographically, and found to be electroreducible at the dropping mercury electrode. The characteristics of the polarographic waves are discussed.

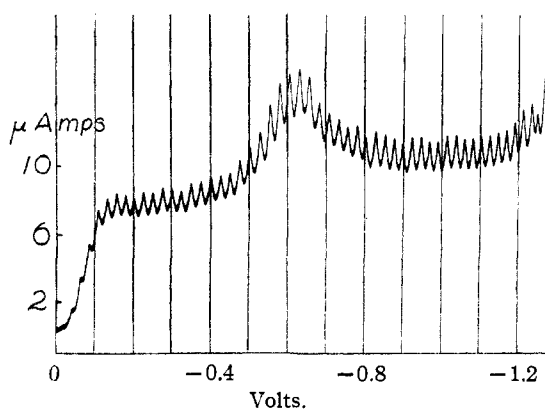2. A molecular compound composed of two molecules of p-hydroxylaminobenzenesulfonamide and one molecule of sulfanilamide, prepared by two different methods, yielded the same melting points and gave exactly the same reduction waves.

3. The bacteriostatic activity of p-hydroxylaminobenzenesulfonamide complex against *Escherichia coli in vitro* in a synthetic medium, was not much greater than that of sulfanilamide.

The System Li₂SO₄–H₂O

BY A. N. CAMPBELL

The complete pressure–temperature–concentration diagram of the system Na₂SO₄–H₂O is very well known.[1] The corresponding system Li₂SO₄–H₂O merits attention since the sulfates of sodium and of lithium, alone among the alkali metals, are able to form hydrates, but no systematic study of this has been made. The aim of the present work was to obtain complete information, as far as possible, of these pressure–temperature–concentration relations.

The literature shows that the monohydrate, Li₂SO₄·H₂O, is very stable and usually constitutes the solid phase in equilibrium with solution. The solubility is but little influenced by temperature between 0 and 100°, although the solubility is greater in cold than in hot water.[2] Solubility measurements have been carried down to −16° by Friend.[3] The most recent work on solubility is that of Appleby, Crawford and Gordon.[4]

Nothing is known of the transition temperature for the reaction: Li₂SO₄·H₂O ⇌ Li₂SO₄ + H₂O (liq.). An approximate calculation of the transi-

tion temperature and pressure can be made from the vapor pressure data of the hydrate by Lescoeur[5] and those of the saturated solution by Appleby, Crawford and Gordon.[4] The result of this extrapolation disagrees widely with the value now reported, but this disagreement was to be expected, since the vapor pressure measurements reach only to 110°.

Experimental

Determination of the Transition Point.—From the known densities of anhydrous and of hydrated lithium sulfate and assuming that anhydrous lithium sulfate dissolves in water with negligible volume change, the expansion accompanying the transformation: Li₂SO₄·H₂O → Li₂SO₄ + satd. solution, is calculated as 8.5%, and this should readily be detected dilatometrically. This calculation neglects the thermal expansion of (superheated) liquid water, which is considerable, so that 8.5% is a lower limit. A dilatometer was prepared from thick-walled hard glass tubing having a stem of coarse capillary. The dilatometer was charged with lithium sulfate monohydrate and aniline as indicator fluid. A thread of pure water was introduced into the top end of the capillary, before sealing off, to give the necessary superincumbent pressure. If this precaution is not taken, the hydrate generates steam at atmospheric pressure at a temperature of 137°, and this may cause the aniline index to break up. From the known dimensions of dilatometer and weight of lithium sulfate monohydrate it was calculated that the transformation would produce a discontinuous linear displacement of the

(1) Cf., for example, Findlay and Campbell, "The Phase Rule and Its Applications," Longmans, London. 8th edit., 1938, pp. 179–181, for bibliography.

(2) Seidell, "Solubilities of Inorganic and Organic Compounds." D. Van Nostrand Co., New York, N. Y., 1940, p. 932.

(3) Friend, *J. Chem. Soc.*, 2330 (1929).

(4) Appleby, Crawford and Gordon, *ibid.*, 1665 (1934).

(5) Lescoeur, *Ann. chim. phys.*, 4, 213 (1896).

index of 3 cm.; the rise of the index per degree rise of temperature was only about 0.05 cm. at low temperatures. As the temperature rose, the expansion per degree increased, perhaps owing to an increased solubility of water in aniline under pressure. There was no sudden expansion, but a region of increased expansion was observed between 233–243°. As will be seen, the true transition temperature lies within this range.

Vapor Pressure Measurements.—The vapor pressure measurements of Lescoeur[5] and of Appleby, Crawford and Gordon[4] are sufficiently accurate in the region to which they apply (up to 110°). The danger lies in extrapolating these measurements for another 130° or so. It was therefore decided to determine experimentally the vapor pressure of the hydrate and of the saturated solution as far as the transition temperature. For this purpose an apparatus was required which would give accurate results for moderate pressures (1 to 30 atmospheres). The apparatus for this purpose, consisting of a stout bulb containing either dry monohydrate or hydrate with saturated solution, together with air, was sealed to a closed manometer. The volume of air enclosed in the manometer, in terms of the length from the end, was determined before mercury was introduced. Before sealing on, the pv value of the manometer was determined from the barometric pressure and the mercury levels. The bulb of the apparatus was then placed in melting ice and the pressure of the air in the bulb determined, assuming the vapor pressure to be negligible at the temperature of melting ice. At higher temperatures the total pressure is read from the closed manometer, with correction for the mercury levels. The vapor pressure is obtained by subtracting from the total pressure the pressure of the air, corrected for the temperature. This method is obviously insensitive if the vapor pressure is small, but when the vapor pressure approaches and exceeds the pressure of the contained air, the accuracy is good. The accuracy decreases again for very high pressures because the air in the manometer is compressed into a very small volume, but this latter disadvantage could be overcome by using a very long manometer: it is not necessary to have the manometer at controlled temperature, beyond the mercury level. The results are contained in Table I.

When these results are plotted in the form log p against $10^6/T$, two sensibly straight lines are obtained intersecting at 235° and a pressure of 21,400 mm. (= 28.2 atm.). The angle of intersection of the curves is very small and there is considerable error in reading the value of $10^6/T$. A more sensitive method is obtained by plotting the ratio p/p' against temperature and reading the temperature at which $p/p' = 1.0000$. This temperature is 233°: the corresponding pressure is 20,290 mm. = 26.7 atm. The difference in vapor pressure of hydrate and saturated solution attains a maximum of 2600 mm. (= 3.4 atm.) somewhere in the range 182–192°.

Transition Point Thermometrically.—A stout glass tube was filled with about 100 g. of dry monohydrate, and sealed off. A narrow glass tube, to carry an iron–constantan thermocouple, was sealed internally into the larger tube so that the junction of the thermocouple was surrounded on all sides by monohydrate. The thermocouple was calibrated from the freezing points of pure lead and of pure tin, and from the boiling point of water. A sensitive potentiometer was used so that the accuracy of temperature measurement was ±0.02°. The tube was suspended vertically in an electric furnace and the temperature raised by a constant amount per minute. A distinct halt in the temperature rise was observed at 232.8°. No corresponding halt was observed on cooling or on raising the temperature again. The reason for this was apparent on examining the cold apparatus: the saturated solution produced had flowed downward to the bottom of the tube and remained there out of contact with the particles of anhydrous lithium sulfate. On refilling the tube with fresh monohydrate and repeating the experiment, the halt was again observed at the same temperature. The transition temperature of lithium sulfate monohydrate, under its own vapor pressure, is therefore 232.8°. The corresponding pressure is 26.7 atm.

Solubility Measurements.—The solubility is known[4,5] with accuracy between 0 and 110°. No measurements are extant above 110° and, since the transition temperature lies at 232.8°, it is of interest to inquire how the solubility varies between 110° and the transition temperature. I used the simple apparatus of Étard[6] in which two bulbs, at an angle of about 90°, are connected by a narrow tube. Saturation is produced in one bulb and then, by tilting, the solution is caused to separate from the solid phase and to run into the second bulb. To increase the efficiency of filtration, the bulbs were joined by narrow capillary and to reduce error due to condensation of vapor the bulbs were kept small. As the bulbs exploded under their own vapor pressure, the apparatus was placed in a heavy steel bomb containing water and the whole immersed in a thermostat. The solubilities were at 142.5°, 22.65; at 186°, 22.7; at 214°, 23.0 grams per 100 grams of solution.

When the data are plotted as in Fig. 1, it appears that the solubility passes through a minimum at 140–160°. Perhaps the accuracy of measurement does not warrant this conclusion but at all events the decrease of solubility from 0 to 100° is not maintained.

TABLE I

VAPOR PRESSURES OF LITHIUM SULFATE MONOHYDRATE AND OF SATURATED SOLUTIONS OF LITHIUM SULFATE

t in °C.	p in mm. (p')	t in °C.	p in mm. (p')
	Hydrate		
114	339	196	7080
131	741	200	7590
137	891	202	8130
158	1990	207	9330
170	3020	211	11200
177	3890	215	12100
182	4470	221	13800
186	5010	225	16600
188	5370	227	17000
190	5890	230	18600
192	6310	232	19100
194	6760		

t	p	$p - p'$	p/p'
	Saturated Solution		
60.15[a]	129.6	107.6	5.88
69.4[a]	197.3	161.8	5.55
84.3[a]	349.9	270.5	4.35
89.65[a]	458.0	351	4.28
99.5[a]	657.7	483.7	3.78
100.1[a]	676.4	492.4	3.68
105.25[a]	799.0	575	3.57
110.35[a]	945.7	657.7	3.29
114	1070	731	3.15
131	1860	1119	2.51
137	2190	1299	2.46
158	3800	1810	1.91
170	5370	2350	1.78
177	6310	2420	1.62
182	7080	2610	1.585
186	7590	2580	1.52
188	7940	2570	1.475
190	8520	2630	1.445
192	8910	2600	1.42
202	10060	1930	1.235
224	18100	1500	1.08
227	18600	1600	1.09

[a] Results of Appleby, Crawford and Gordon.[4]

(6) Étard, Ann. chim. phys., [7] 2, 524 (1894).

I attempted to investigate the solubility above the transition temperature by sealing up slightly unsaturated solutions in stout capillary tubing and noting the temperature at which crystals appeared, but such tubes invariably exploded. One tube containing 20.0% Li₂SO₄ remained clear up to 311°, so the solubility has not decreased appreciably up to this temperature.

The Ice Line.—This curve has been determined by Dreyer[7] up to 4.55% Li₂SO₄. My results are in good agreement as far as his measurements go. I used the technique described by Davison, van Klooster and Bauer[8] in which the equilibrium liquid phase is analyzed. The results are contained in Table II.

TABLE II

FREEZING POINTS OF SOLUTIONS OF LITHIUM SULFATE

Concn. in g. of Li₂SO₄ per 100 g. of soln.	Freezing point in °C.
4.072	− 1.735
7.791	− 3.30
11.30	− 5.11
14.33	− 7.04
17.67	− 9.67
21.95	−14.65
24.85	−18.45
27.1	−21.4
Eutectic	−23.0

The last determination of the above table was made by preparing a saturated solution at −15°. This solution was found by analysis to contain 27.1% Li₂SO₄. It was submitted to thermal analysis, using a copper–constantan thermocouple and a sensitive potentiometer. After slight supercooling, this solution separated ice at −21.4°, fol-

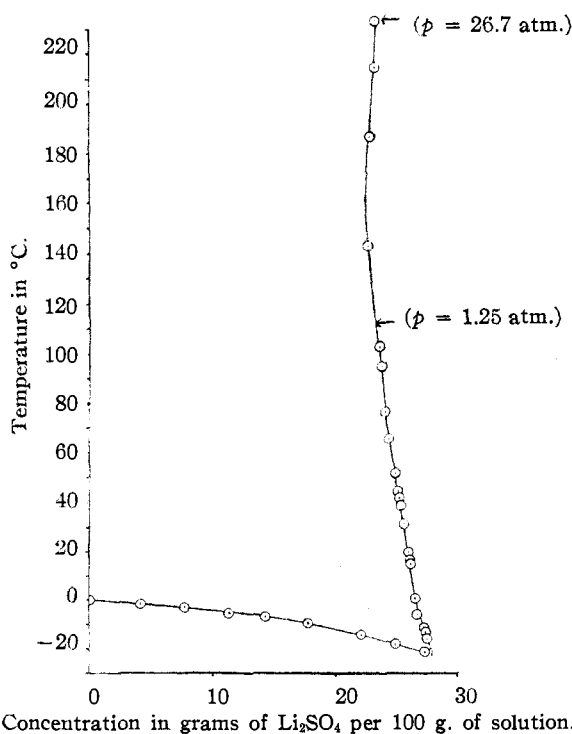lowed by eutectic freezing at −23.0°. All the ice points lie on a smooth curve, which becomes increasingly convex to the axis of concentration, as the concentration increases. If this curve is extrapolated to intersect Friend's (extrapolated) solubility curve, intersection is found to occur at −23° and 27.9% Li₂SO₄. There is no doubt of the eutectic temperature; the eutectic concentration rests on two uncertain extrapolations. It is virtually impossible to determine the eutectic directly, because of the impossibility of preparing a solution of 27.9% concentration, at any other temperature than the eutectic itself.

According to Étard,[6] the solubility increases rapidly from the eutectic temperature, passes through a maximum below 0° and subsequently decreases. The latest work in this region is that of Friend, who finds that the solubility decreases progressively from the lowest temperature of measurement (−16.0°); he believes, however, that the dihydrate, Li₂SO₄·2H₂O, exists at low temperatures. I have used Friend's figures in completing the diagram.

Discussion

The complete diagram is represented in Fig. 1. The data are my own, except those for the solubility between −16 and 110°, which are due to Friend.[3] The eutectic temperature of the system Li₂SO₄–H₂O is −23.0°. On the basis of a somewhat doubtful extrapolation (shown dotted on the equilibrium diagram) the eutectic composition results as 27.9% Li₂SO₄. As pointed out elsewhere, it is practically impossible to make a direct determination of the eutectic composition. If the hypothetical portion of the curve is provisionally accepted, it would appear that the solubility of lithium sulfate is a maximum at the eutectic temperature, after which it decreases continuously to 22.6% at 142°. There is then a slight increase in solubility up to the transition point of the change Li₂SO₄·H₂O → Li₂SO₄ + H₂O (liq.), which occurs at 232.8° under the system's vapor pressure of 26.7 atm.

On the curve as drawn by me there is no discontinuity corresponding to the formation of a second solid phase at low temperature. Nevertheless, Friend[3] claims the existence of a second hydrate, Li₂SO₄·2H₂O, on the basis of the rather crude method of direct analysis of the solid phase. To test this, I carried out dilatometric experiments on the system Li₂SO₄ + water, leaving the dilatometer at −12° overnight to induce formation of the hypothetical hydrate, and taking the temperature up and down between the limits −13.8° and −2.2°, but I could not detect any discontinuity. It is quite possible, however, that owing to metastability the dihydrate did not form in the dilatometer. Still further to test this matter I have investigated the equilibrium diagram of the system: Li₂SO₄–LiCl–H₂O, at −12.25°. The results are given in Table III.

Fig. 1.—Equilibrium diagram: Li₂SO₄–H₂O.

(7) Quoted in Gmelin's "Handbuch," System Number 20, p. 212 (1926).

(8) Davison, van Klooster and Bauer, "Laboratory Manual of Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 56.

TABLE III

THE SYSTEM Li₂SO₄–LiCl–H₂O AT −12.25°

Solution		Wet solid phase	
%Li₂SO₄	%LiCl	%Li₂SO₄	%LiCl
22.00	3.16	66.91	1.03
16.02	7.10	64.63	2.25
6.18	14.60	64.84	3.92
0.38	25.03	71.81	8.65

These data are plotted in Fig. 2. The invariant point lies at a concentration in solution of 0.38% Li_2SO_4 and 25.03% LiCl, and the solution is saturated with respect to $Li_2SO_4 \cdot H_2O$ and LiCl. The tie-lines show clearly that the stable solid phase is the monohydrate throughout the concentration range investigated; it is possible that the dihydrate, if it exists, is dehydrated to monohydrate by less than 3.16% LiCl.

Summary

1. For the system Li_2SO_4–H_2O, the following data have been elucidated: (a) The transition point of the change: $Li_2SO_4 \cdot H_2O \rightleftarrows Li_2SO_4 + H_2O$, which is shown to lie at 232.8° and a pressure of 26.7 atm. Three independent methods were used, viz., the dilatometric, the method of vapor pressure and the thermometric. (b) The solubility between 110 and 214°. (c) The ice-line.

2. The existence of a higher hydrate of lithium sulfate, possibly $Li_2SO_4 \cdot 2H_2O$, is considered to be doubtful. The technique involved was (a) dilatometric, and (b) a study of the equilibrium diagram of the system Li_2SO_4–LiCl–H_2O, at
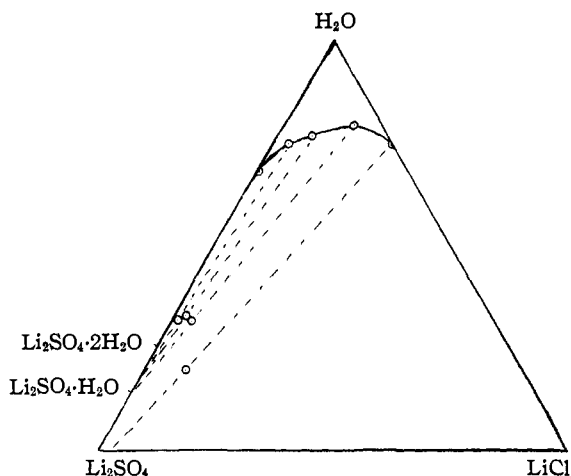

Fig. 2.—The system Li_2SO_4–LiCl–H_2O at −12.25°.

−12.25°. The existence of the dihydrate cannot, however, be considered as entirely disproved.

WINNIPEG, CANADA   RECEIVED MAY 29, 1943

Cyanates and Thiocyanates of Germanium, Phosphorus, Sulfur and Chromium

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

The preparation and properties of cyanates or thiocyanates, or both derived from boron bromide, silicon tetrachloride, phosphorus, arsenic and antimony trichlorides and phosphoryl chloride have recently been investigated[1,2] in this Laboratory. The successful preparation of silicon tetra(iso)cyanate suggested that germanium tetrachloride also would react completely with silver isocyanate. The formation of phosphoryl isocyanate,[2] though in low yields, gave promise that thiophosphoryl (iso)cyanate might be obtained, though in even lower yields and smaller thermal stability. In addition, sulfur monochloride, thionyl chloride, sulfuryl chloride and chromyl chloride provided an interesting range of possibilities as yet but little explored.[3]

Germanium Isocyanate.—The preparation involved 18.9 g. of germanium tetrachloride, 60 g. of powdered silver (iso)cyanate, and 100 ml. of pure benzene. Upon gradual addition of the chloride there was considerable rise in temperature. Two hours' reflux and shaking were sufficient for essential completion of the reaction. Upon filtration and careful washing of the silver salt with hot benzene, a very pale yellow solution was obtained. Upon removal of benzene at atmospheric pressure nearly 10 ml. of a pale yellow liquid remained. Colorless germanium isocyanate was obtained by distillation at 128° and 62 mm. both uncorrected; the first 6 ml. was collected and used for all physical measurements. Subsequently, this sample was found to distil entirely between 203.7 and 204.2°

(corrected to 760 mm.), using a thermometer calibrated with a middle fraction of benzoyl chloride. No change in boiling point, melting point or refractive index was observed in successive fractions. It has been shown[4] that the boiling point of the isocyanate of a non-metal exceeds that of the corresponding chloride by 31°, on the average, for each isocyanate group. As germanium chloride boils at 83°, germanium isocyanate ought to boil at 207°, in good agreement with the observed boiling point 204°.

Analysis of redistilled material followed. A weighed sample in a weighed crucible with cover was carefully hydrolyzed by slow addition of water. Time was allowed for complete hydrolysis; a trace of nitric acid was added and the mixture stirred with a tiny glass rod. Careful evaporation and ignition gave germanium dioxide. Results from tenth-gram samples of germanium isocyanate were as follows: %Ge 29.6, 30.4, av. 30.0; calculated value 30.17%. The molecular weights were obtained by means of the Dumas method: found 247 and 248; calculated 240.7.

Germanium isocyanate is a colorless liquid which showed no tendency to pass into a more stable solid phase. When it was treated with water, there was a strong effervescence, typical of cyanates, but the hydrolysis appeared somewhat less rapid than that of silicon isocyanate. Upon cooling, the liquid became very viscous, and solidified only at −65°. It melted quite sharply at −8° ± 0.5°. The density was found to be 1.760 by delivery from a calibrated 1-ml. pipet at 30° and also by use of a micropycnometer at 25°. Refractive index, read on an Abbe refractometer with thermostated prism, was 1.4858 at 20°. The boiling point (760 mm.) is 204° ± 0.4°. Boiling points at four other pressures were measured by a dynamic method in an all-glass system with a calibrated thermometer. The equation for vapor pressure is log p = 8.6578 − 2757/T so that λ = 12,600 cal. and λ/T_b = 26.4 cal./deg./mole.

(1) Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940).

(2) Anderson, ibid., **64**, 1757 (1942).

(3) Dixon, J. Chem. Soc., **79**, 541 (1901).

(4) Ref. 2, p. 1759.