37. *Specific Conductivity Measurements directly related to Solubilities with Special Reference to Calcium Sulphate (Anhydrite) Solutions.*

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The specific conductivity, κ, has been measured in aqueous calcium sulphate solutions, varying in concentration up to saturation with gypsum in the temperature range 20—50°. By considering rates of variation of conductivity with temperature for the different concentrations, the specific conductivities have all been converted into values corresponding to 20°. An equation has been derived to relate these adjusted values to concentration and hence to get solubilities directly from specific conductivity data for saturated solutions of anhydrite. This direct method has been applied to find solubilities of anhydrite in the range 20—35°.

HILL [1] casts considerable doubt on the trustworthiness of many of the solubility data for calcium sulphate (anhydrite), the chief cause of doubt being the absence of any real evidence of the existence of equilibrium in the saturated systems used although generally considerable time was given for this to occur. He comments on the dearth of information on the solubility of anhydrite at <*ca.* 50°, and earlier [2] he concluded that it was in harmony with the van't Hoff mean valency rule that anhydrite should take many days in reaching saturation equilibrium. He also showed that, above 42°, gypsum has a greater solubility than anhydrite, gives constant reproducible solubilities, and does not decompose. Such

[1] Hill, *J. Amer. Chem. Soc.*, 1937, **59**, 2242.
[2] *Idem, ibid.*, 1934, **56**, 1072.

solutions are considered metastable. Hulett and Allen,[3] incidentally to some determinations of the solubility of gypsum by chemical analysis, measured the specific conductivity of saturated solutions at temperatures up to 100° and concluded that equilibrium was attained in no more than $1\frac{1}{2}$ hours.

Posnjak [4] considers that disagreement among different authors is due to inefficient filtration when withdrawing samples of saturated solution for analysis, suspended particles being dissolved on dilution. He used both naturally occurring anhydrite and samples prepared by heating gypsum and concluded that the solubility varied with the origin of the anhydrite, a conclusion supported by Hill.[1]

In the present work an attempt was made to find solubilities of anhydrite directly from specific conductivities of the saturated solutions at 20—35°, by computation, and without chemical analysis. It was also hoped to find information about the time required to reach saturation equilibrium. Hill [1] concluded that the transition temperature for the change gypsum $\rightleftharpoons$ anhydrite is 42° $\pm$ 1° and that, although anhydrite should be metastable below 42°, it changes so slowly that steady and reproducible metastable solubilities can be measured. By using conductivity cells of known cell constants to contain saturated solutions, κ_t (*t* in °c) can be measured quickly and frequently without disturbing the saturating system by withdrawal of samples.

Conductivities of saturated calcium sulphate solutions at different temperatures will show variations due to changes in both concentration and ionic mobility, and a method is required to adjust κ_t values to one temperature only. Table 1 gives values for κ_t over a range of temperature, for seven unsaturated solutions. The seven linear graphs of conductivity against temperature have a common constant characteristic slope, A, and, with 20° as an arbitrary reference temperature, $\kappa_t = \kappa_{20} + (t - 20)A$ generally. The slope A varies with concentration and if its value could be found for any concentration then κ_{20} values for all solutions would be available. Plotting A against κ_{20} for the seven concentrations gives another linear graph, $A = b\kappa_{20} + a$ (Fig. 1), fitted by " least squares." The constants, found from the graph, are $a = 1.743 \times 10^{-6}$ and $b = 1.994 \times 10^{-2}$. Substitution for A in the foregoing equation for κ_t gives

$$\kappa_{20} = [\kappa_t - 1.743 \times 10^{-6}(t - 20)]/[1 + 1.994 \times 10^{-2}(t - 20)] \quad . \quad . \quad (1)$$

This equation covers the whole concentration range used and should enable any κ_t value to be converted into κ_{20} by which different solutions could be compared. Also the equation can be used to treat κ_t values for saturated solutions, measured at any temperature. A plot of κ_t against concentration at each experimental temperature appeared to give a parabola, an equation for which was found from our results. For seven different temperature the equations, of the form Concn. (wt.%) (*c*) = $A + B\kappa_t + D\kappa_t^2$, differed somewhat but correction of κ_t to κ_{20} by our equation reduced this disparity, and the mean of these corrected equations gave

$$c = -0.0064 + 83.26\kappa_{20} + 10,630\kappa_{20}^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Equation (2) is considered to be quite general and applicable to any solutions within the temperature range 20—50° and has been used to find solubilities of anhydrite in the range 20—35°. Anhydrite changes so slowly between 20° and 35° that steady and reproducible conductivities can be measured, solubilities found, and the time to reach saturation explored. Hulett,[5] experimenting only at 25°, also used a parabolic equation to connect κ_{25} with concentration but the expression is only of limited application. Roller,[6] studying saturated anhydrite solutions at 20°, reported a progressive rise in the conductivity to a maximum and, after a pause, a very slow decrease. The maximum was considered to be the true equilibrium value and the subsequent decrease was ascribed to slow hydration, causing a slight change in solubility.

Measurements of κ_t for certain calcium sulphate solutions led Kohlrausch [7] to propose

[3] Hulett and Allen, *J. Amer. Chem. Soc.*, 1902, **24**, 667.
[4] Posnjak, *Amer. J. Sci.*, 1938, **35**, 247.
[5] Hulett, *Z. phys. Chem.*, 1903, **42**, 577.
[6] Roller, *J. Phys. Chem.*, 1931, **35**, 1132.
[7] Kohlrausch, *Z. phys. Chem.*, 1908, **64**, 129.

an empirical expression for referring all values to a common temperature (18°), and he related these corrected values with concentration through infinite-dilution equivalent conductivity, an indirect procedure.

<div align="center">EXPERIMENTAL</div>

Chemicals used were all at least of "AnalaR" purity. Anhydrite was prepared and dried by Hill's method; [2] analysis showed 100% purity.

Conductivity Cells.—Two cells (Fig. 2), designed specially for use with saturated solutions, had recesses to hold and protect the electrodes of thick platinum foil. The leads from the cell were connected through mercury to the electrical measuring circuit. The electrodes were cleaned and platinised by the methods of Popoff, Kunz, and Snow.[8] Each cell carried a tightly fitting rubber stopper with a $\frac{1}{4}''$ steel ball-race bedded centrally. A Pyrex-glass paddle stirrer, held in the ball-race, rotated in a fixed position. The cells were immersed in a water-thermostat bath in aluminium holders.

FIG. 1.

FIG. 2.
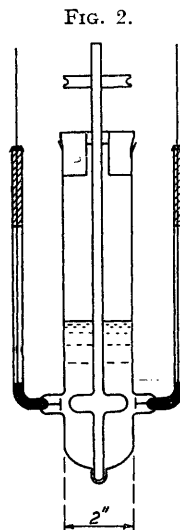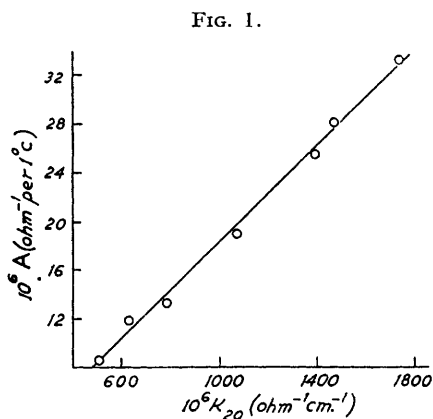
The thermostat was heated by a 250 w spiral immersion heater. A toluene–mercury temperature regulator incorporated a proportioning head, and the heater was coupled to an electronic relay; this gave temperature control better than $\pm 0.01°$ at 25°.

Electrical Circuit.—Accurate resistance measurements were made with a Mullard bridge, type GM. 4140, extended by a four-decade inductance-free resistance, range 0—12,000 ohms by single units. An electron-beam indicator tube gave the balance point visually. Alternating current (1000 cycles sec.$^{-1}$) was supplied.

Cell Constants.—Jones and Bradshaw's methods [9] were followed in preparing the "demal"* potassium chloride solution used in finding the cell constants required to convert resistances into specific conductivities. Customary practice as to washing and rinsing was followed. The glass stirrers in the cells were stopped and raised while the resistance was measured; 20 mins. were allowed for equilibration of temperature before measurements of resistance.

Calcium Sulphate Solutions.—Seven unsaturated solutions were prepared from saturated gypsum solution and analysed by the oxalate–permanganate method. 150 c.c. of each solution were used in each conductivity cell. All seven solutions were similarly treated at 5° intervals up to 50°. Results (Table 1), corrected for distilled water, include densities, determined with pyknometers calibrated with distilled water. Thus compositions are expressible either by weight or volume. The distilled water had a specific conductivity between 2×10^{-6} and 4×10^{-6} mhos over the whole temperature range.

To extend the concentration range, saturated gypsum solutions have also been similarly examined. They were prepared in conductivity cells by adding 3 g. of gypsum to 150 c.c. of

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* A "demal" solution was defined by Jones and Bradshaw [9] as one containing 1 mole of a salt per cubic decimeter of solution at 0°.

[8] Popoff, Kunz, and Snow, *J. Phys. Chem.*, 1928, **32**, 1056.

[9] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780.

distilled water in a thermostat. Stirring was continuous, except when resistances were measured, and readings were continued until constant ($\not> ca.$ 3 hr.).

TABLE 1. *Conductivities* $(C = 10^6 \kappa_t,\ ohm^{-1}\ cm.^{-1})$ *and densities* (d) *of* $CaSO_4$ *solutions.*

CaSO₄ concn. (wt. %):	0·0332		0·0611		0·0689		0·1029	
Temp.	d	C	d	C	d	C	d	C
20·0°	0·99854	471·8	0·99924	740·4	0·99906	822·9	0·99930	1145
25·0	0·99750	522·9	0·99764	818·9	0·99770	904·7	0·99803	1258
30·0	0·99610	576·8	0·99626	890·5	0·99640	997·7	0·99656	1370
35·0	0·99459	630·2	0·99470	972·8	0·99465	1092	0·99500	1506
40·0	0·99254	684·8	0·99276	1056	0·99284	1184	0·99315	1638
45·0	0·99062	738·5	0·99122	1138	0·99123	1277	0·99135	1759
50·0	0·98848	793·3	0·98853	1216	0·98860	1367	0·98903	1881

CaSO₄ concn. (wt. %):	0·1312		0·1504		0·1620	
Temp.	d	C	d	C	d	C
20·0°	0·99964	1413	0·99976	1574	0·9993	1696
25·0	0·99849	1569	0·99863	1739	0·99874	1874
30·0	0·99704	1725	0·99708	1890	0·99732	2050
35·0	0·99554	1877	0·99563	2045	0·99574	2228
40·0	0·99349	2031	0·99366	2224	0·99372	2410
45·0	0·99166	2181	0·99215	2382	0·99194	2583
50·0	0·98898	2327	0·98953	2539	0·98960	2755

TABLE 2. *Conductivity* $(C_1 = 10^6\kappa_t,\ C_2 = 10^6\kappa_{20},\ ohm^{-1}\ cm.^{-1})$, *solubilities* (S), *and densities* (d) *of saturated gypsum solutions.*

Temp.:	20°	25°	30°	35°	40°	45°	50°
C_1	1966	2216	2433	2659	2882	3079	3268
C_2	1966	2006	2014	2026	2035	2025	2012
S (wt. %)	0·2040	0·2055	0·2073	0·2082	0·2102	0·2078	0·2048
d	1·00040	0·99915	0·99778	0·99620	0·99426	0·99244	0·99000

Solubilities (Table 2), found by direct analysis, are given, with κ values, the latter agreeing with those reported by Kohlrausch.[7] Samples for analysis were withdrawn through sintered-glass filters (porosity 4) (cf. Posnjak [4]). The solubilities at 45° and 50° are metastable for the solid phase gypsum as Hill [2] found at 45° and 60°.

From the entire range of conductivities, equation (2) was derived and applied to find solubilities of anhydrite from κ_t values for the corresponding saturated solutions without chemical analyses. Probably the equation is applicable outside the range 20—50°.

Solubility of Anhydrite.—Conductivities of saturated anhydrite solutions were measured as with saturated gypsum solutions and use of equations (1) and (2) gave solubilities (Table 3). The time to reach saturation equilibrium was shown when the conductivity reached a maximum (cf. Roller,[6] who reported the identical value for the conductivity at 20°).

TABLE 3. *Conductivities* (C), *solubilities* (S), *and time to reach equilibrium in saturated anhydrite solution.*

Temp.:	20°	25°	30°	35°
C_1	2637	2780	2897	3026
C_2	2637	1520	2401	2309
S (wt. %)	0·287	0·271	0·255	0·243
Time (hr.)	24	55	95	150

Comparison of results with those of other workers is possible only for individual temperatures. Hill,[1] using the analytical method, gives the same solubility at 35° as that now reported but, whereas he considered the time to reach equilibrium to be at least 28 days, we find that nowhere did it exceed 150 hr. Possibly such times are influenced by the efficiency of stirring. Posnjak [4] gives solubilities in good agreement with the present results but shows that results depend on the origins of the anhydrite used. For comparison, a sample of natural anhydrite (from Nottingham) was also used in the present work. It required a shorter time to reach equilibrium and gave a slightly lower solubility than the anhydrite prepared by Hill's method.[2] We regard the latter as the most satisfactory in giving anhydrite from which reproducible results are obtainable.

Hulett and Allen [3] found that a saturated solution containing solid gypsum attacked glass slightly at 50° and we find that with solid anhydrite in a saturated solution a slight and slow attack on glass occurs at about 40°.

The data for saturated gypsum (Table 2) show a maximum solubility at 40°, and the κ_{20} values run exactly parallel. This agrees with well-established results for the solubility of gypsum (see, *e.g.*, Hulett and Allen [3]).