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STUDY ON THE EQUILIBRIA AND PROPERTIES OF BRINES

G.Conti[†], P.Gianni[†], G.F.Nencetti[†], L.Petarca[†], M.R.Tinë[†],
N.Vatistas[†]

[†] Institute of Physical Chemistry, University of Pisa, Italy

[†] Institute of Industrial and Applied Chemistry, University of Pisa,
Italy

Brines at high temperatures and with a high salt content can, in principle, be exploited for many purposes including the production of electric energy, the supply of district heating and the recovery of those chemical compounds which are of commercial interest.

Obviously, in order to examine the different exploitation possibilities of such brines to determine the best alternatives and consequently the most suitable technological cycles for the complete utilization of the resource, it is essential that sufficient information on the characteristics of the salt composition of the system and, in particular, on the equilibria in solution is available. This information must refer to all the thermodynamic properties, e.g. heat capacity, latent heat, vapour pressure, etc.

The problem of obtaining such information arises whenever a new geothermal resource is discovered as one manifestation can vary considerably from another. This is shown by the data given in Table I which refer to some Italian geothermal areas.

The complexity of the systems involved means that it is unrealistic to attempt a theoretical approach to this problem. It was, therefore, decided to initiate an experimental research program in order to obtain data which could be compared with the data already published and could be used to determine the

values which are still lacking in the literature.

Although the development of theoretical prediction methods had been excluded a priori, the reliability of certain semi-empirical relations for the extrapolation of the available da

TABLE I

Chemical Composition of Brines from some Italian geothermal fields.

	Cesano 5 (1)	Cesano RCl (2)	Latera 2 (3)	Latera 2 (4)	Piancasta gnaio 20 ^o (5)	Cesano 1 (6)
Total Salinity (mg/l)	101,000	167,376	8,595	7,563	15,242	350,000
Ca ⁺⁺	9.5	60.36	10.8	289	-	110
Mg ⁺⁺	6.0	10.69	3.2	10.45	-	15
Na ⁺	22,000	52,142	2,450	1950.0	1,400	57,000
K ⁺	15,800	33,833	351	286.0	282	77,000
Li ⁺	80	-	10	9.3	-	180
Cs ⁺	62	-	3	-	-	50
Rb ⁺⁺	116	-	2.5	0.74	-	350
Fe ⁺⁺ +Fe ⁺⁺⁺	7.2	-	-	3.0	-	0.7
NH ₄ ⁺	206	31.17	24.8	67.84	136.4	100
Al ⁺⁺⁺	-	-	-	-	-	-
As ⁺⁺⁺	440	-	147	77.0	60	5.0
Cl ⁻	26,530	17,313	2,815	2,292	2,325	27,000
SO ₄ ⁻	24,450	76,638	415	347	-	180,000
NH ₃ (total)	-	29.41	23.4	64	129	-
CO ₂ (total)	3,365	2,520	849	1,418	44	1500
H ₂ S (total)	194	-	40	12	12	trace
CO ₂ (gas)	-	-	370	390	44	-
Boron as H ₃ BO ₃	11,265	7,892	1,600	1,271	13,958	7,000
SiO ₂	133	140	440	247	1,350	130
pH	7.95	8.35	7.94	7.2	7.1	7.5

(1) Sample taken 14-15 May 1979.

(2) Sample extracted with airlift, 12/8/77.

(3) Mean values of five samples taken during delivery.

(4) Water taken using sampler (total fluid), 12/6/80.

(5) Analyses of samples of entrained water, 12/10/80.

(6) Mean values for analyses of water delivered.

ta was analysed with reference to at least some of the properties to be recognized. The priority of the properties to be recognized changes according to the particular application of the geothermal resource. The various aspects of this problem are listed in the following points.

a) Chemical exploitation of the resource.

This type of exploitation can be employed directly on brines at temperatures which are considered unsuitable for energy or heat production. It can also be applied to brines at high temperatures after they have been first exploited for electric energy production.

Examining the compositions reported in Table I, it can be seen that the brines appear particularly interesting for the recovery of potassium salts and boric acid and also of sodium sulfate, even if it is rather doubtful whether this last salt is of any real commercial interest.

It should be remembered that although the recovery of salts may be economically advantageous it also gives rise to many minor problems and difficulties connected with the disposal of the exhausted brines.

A number of processes for the recovery of potassium salts from brines have been described in the literature, e.g. precipitation as perchlorate (1) (2) or potassium salt of dipi-crylamine (3-8) or in the form of double salts such as synginite or alum or recovery using high selectivity ionic exchange resins (9-13). The most practical process from the operational viewpoint, however, seems to be the utilization of fractional crystallisation. This has been confirmed by technical and economical analyses of different processes. In order to use this method, it is essential to have a full knowledge of the equilibria in solution in the system in addition to the other thermodynamic properties.

b) Thermal exploitation of the resource.

When there is no interest in the recovery of the saline products, the main information necessary is the total solubility curve. This curve represents the separation of the salts as the temperature of the brine decreases. Obviously, all the other thermodynamic properties must also be known.

c) Exploitation of the resource to produce electric power.

The observations made above in point b) are also valid for this.

In order to study the most suitable process to be used for the exploitation of the resource it is important to have as complete a picture as possible of the salt equilibria in the aqueous phase and also of the gas solution equilibria as these have a direct bearing on the possibility of corrosion or scaling during the delivery.

In the experimental research program described in this paper all these factors have been considered and the first results are given here.

As the research program has been conducted from a practical rather than a theoretical stance, the measurements have often been performed adopting standards of precision and accuracy which, while completely acceptable on the technical level, would certainly be inadequate if judged from a scientific view-point. However, as the program has progressed, equipment has been designed, developed and tested so that it will be possible in the near future to achieve results which are completely satisfactory also on the scientific level.

COMPLEX EQUILIBRIA IN SOLUTION

Studies, described in detail elsewhere (4), have been conducted to examine the quaternary system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-KCl-NaCl}$; these are the predominating salts in the brine of Cesano 1 well. Data on this system, limited to temperatures below 100°C , have already been published. Our experience so far is limited to verifying the data reported in the literature for this system and to investigating the influence of the other species such as boric acid.

We used a very simple apparatus, represented in Fig. 1, consisting of a container of pyrex glass composed of a central piece with a sinterized glass filter (G1 porosity) and two 100 ml. flasks connected by means of spherical joints.

The water and an excess of the predicted solid phases were loaded into the lower part of the apparatus and the system was stirred

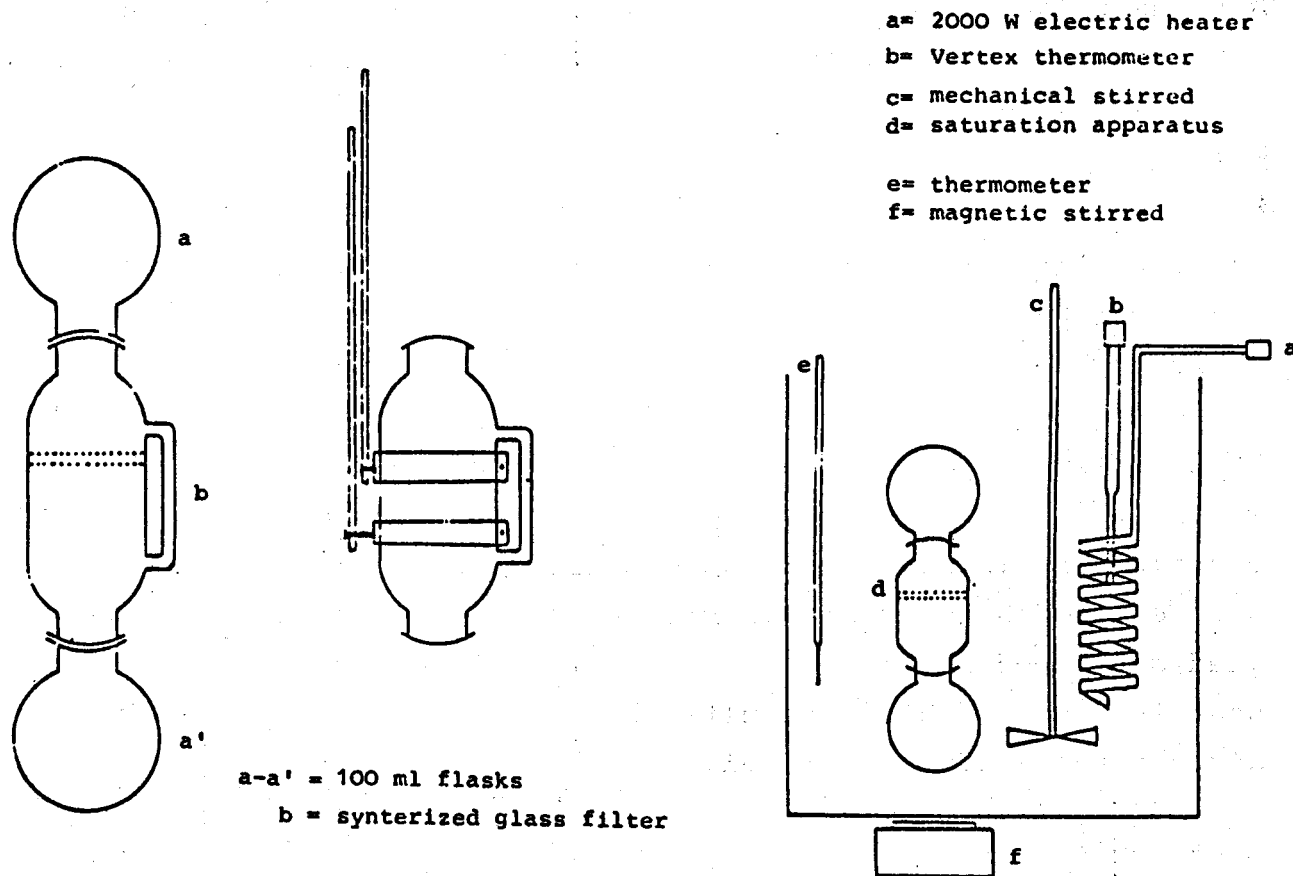


Fig. 1. Apparatus for solubility measurements.

red by a magnetic stirrer. The device was placed inside a thermostatic bath which maintained a chosen temperature within $\pm 0.05^\circ\text{C}$. When sufficient time had elapsed to ensure that equilibrium had been reached, the equipment was reversed without removing it from the bath. The clear solution was separated from the residual solid phase by filtration through the septum and then chemically analysed in order to determine the concentrations. Fig.2 plots the path of our experimental points against that derived from the published data. The influence of the presence of other chemical species is, however, of great relevance. In fact, if boric acid is present in the system the diagram changes considerably. This is shown by Fig.3 which illustrates a Jänecke diagram at 100°C and shows the shifting in position of the point of equilibrium of glaserite, sodium chloride and potassium chloride. The presence of boric acid causes the point to shift towards zones with higher sulfate and potassium ion concentrations, particularly at higher temperatures. In addition, there is a strong increase in the solubility of both the species of the system $\text{Na}^+ - \text{K}^+ - \text{SO}_4^{--} - \text{Cl}^-$ and of the boric acid, see Fig.4.

From our experience with simplified systems, we have concluded that although such systems can be to some extent indicative of general behaviour, they may well be inadequate for a complete understanding of the real system. Furthermore, the problem of studying the system at higher temperatures is still unresolved and the implementation of a first autoclave has not proved satisfactory.

INTEGRAL SOLUBILITY DATA

In addition to the composition and nature of the separated solid phase, the main parameters which should be known are the temperature at which the separation of the solid phase begins and the total amount of solids separated from the brine as the temperature decreases. As apparatus has not yet been developed which is capable of operating at elevated temperatures and pressures, we

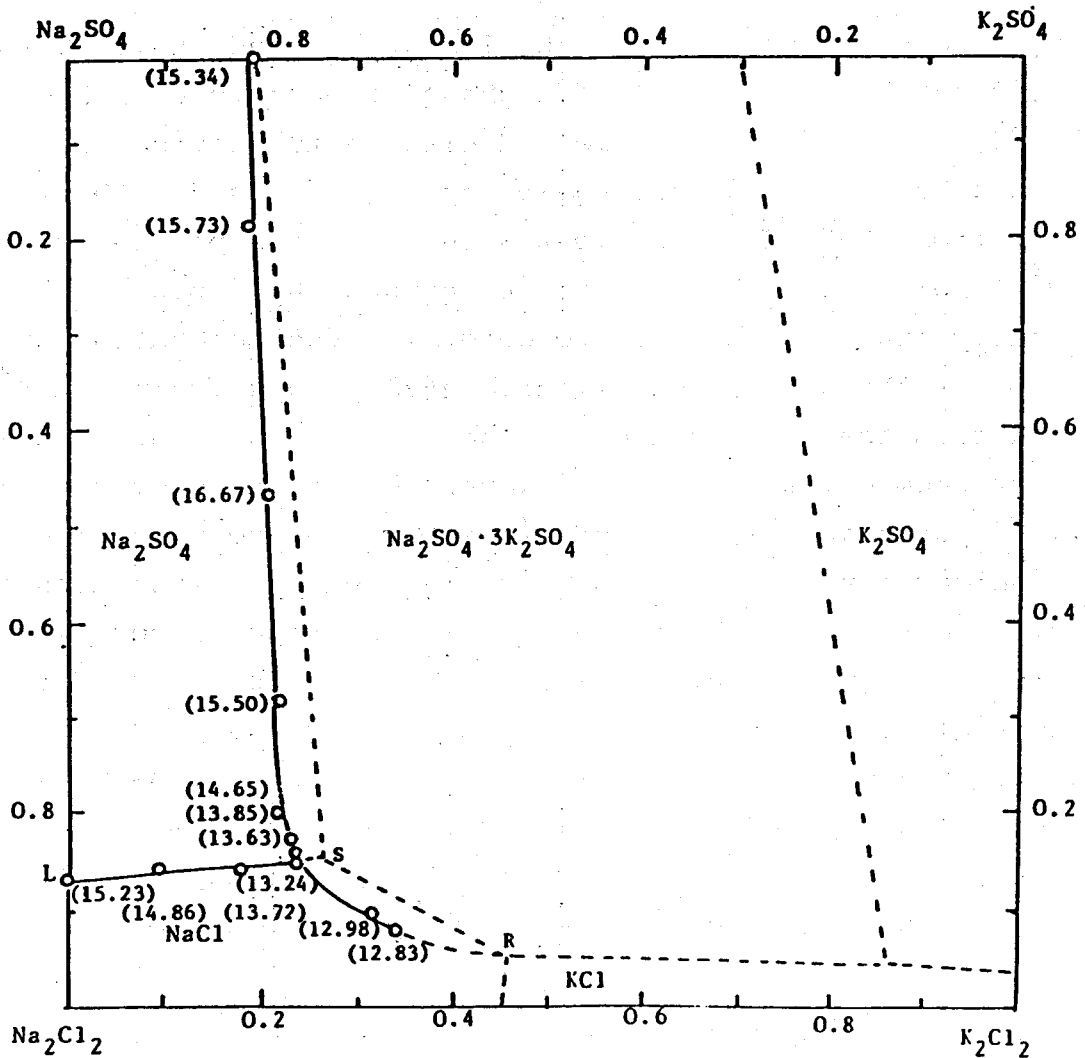


Fig. 2. Janecke diagram at $T = 75^\circ\text{C}$.

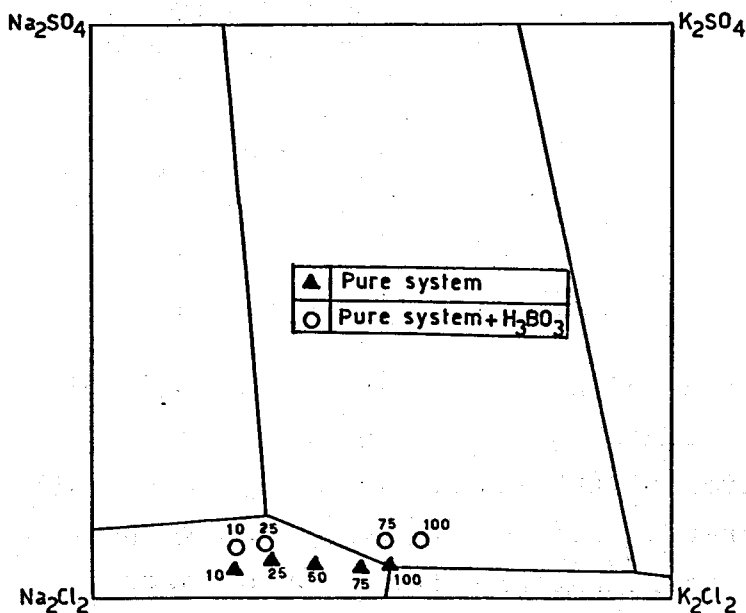


Fig. 3. Janecke diagram at 100°C ; influence of the presence of boric acid.

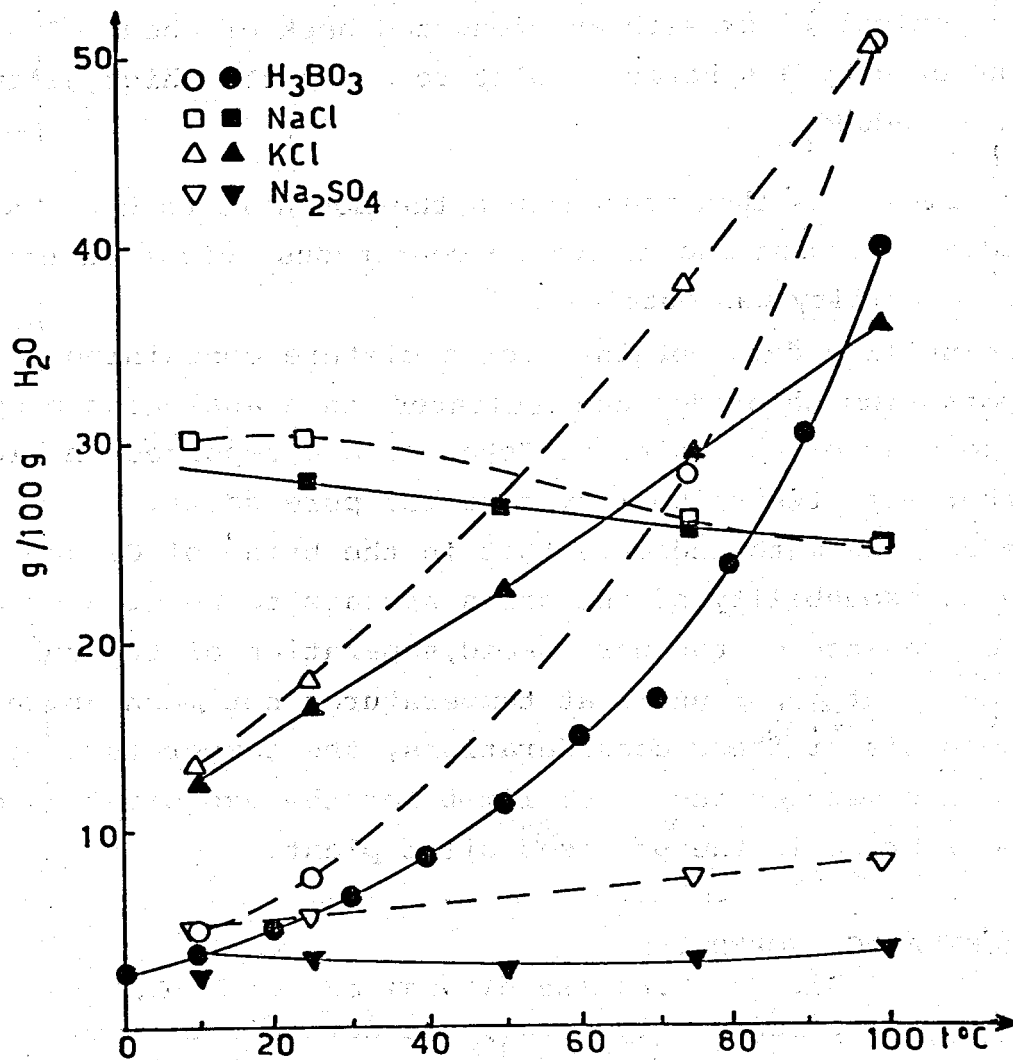


Fig. 4. Solubility vs temperature of Na_2SO_4 , KCl , $NaCl$ and H_3BO_3 when boric acid is absent (black points) or present (white points) in the system.

have performed measurements below 100°C by using a simple apparatus. The desired salt composition was weighed and introduced into a conical flask with an elongated neck of about 20 cm which is connected by a spherical joint to a burette which allows water to be added.

The flask was then placed in a thermostatic bath and water was added, keeping the system in continuous agitation until total solubility was obtained.

The solubility data obtained for a mixture containing sodium and potassium chlorides and sulfates in a analogous proportion to that of the brine of Cesano 1 are reported in Fig. 5 together with the solubility data for pure salts.

These data seem to indicate that in the brine of Cesano 1, where the solubility of the salts appears to be greater owing to the presence of the boric acid, separation of the solid phase should not occur until at temperatures not much above 100°C. On the basis of these considerations, the temperature of 125°C has been chosen as the lower limit for the exploitation of the Cesano 1 brine in the proposed pilot plant.

THERMODYNAMIC PROPERTIES

From the experimental viewpoint, the determination of certain properties, such as steam pressure for example, presents no particular difficulties as long as suitable equipment is available. The theoretical prediction is obviously far more complex. Neither are there any particular problems, from the practical side in measuring the latent heat of the evaporation of water as this is influenced very little by the salt concentration. The measurement of the heat capacity is a much more important and complex problem.

There is a notable lack of published data concerning brines at elevated temperatures and concentrations. Bromley (15), Silvester and Pitzer (16), and Tanner and Lamb (17) have measured the dependence of the heat capacity on the concentration. These authors, however, were working with a limited range of tempera

tures and concentrations and generally restricted their studies to simple systems.

From these considerations, there emerges a clear necessity for the collection of an extensive body of experimental data.

The work began by measuring the heat capacity of a series of multi-component salt mixtures and of all the single electrolyte solutions contained in them in order to find suitable correlations which could be used to predict the heat capacity of such mixtures over a much wider range of temperatures and total con

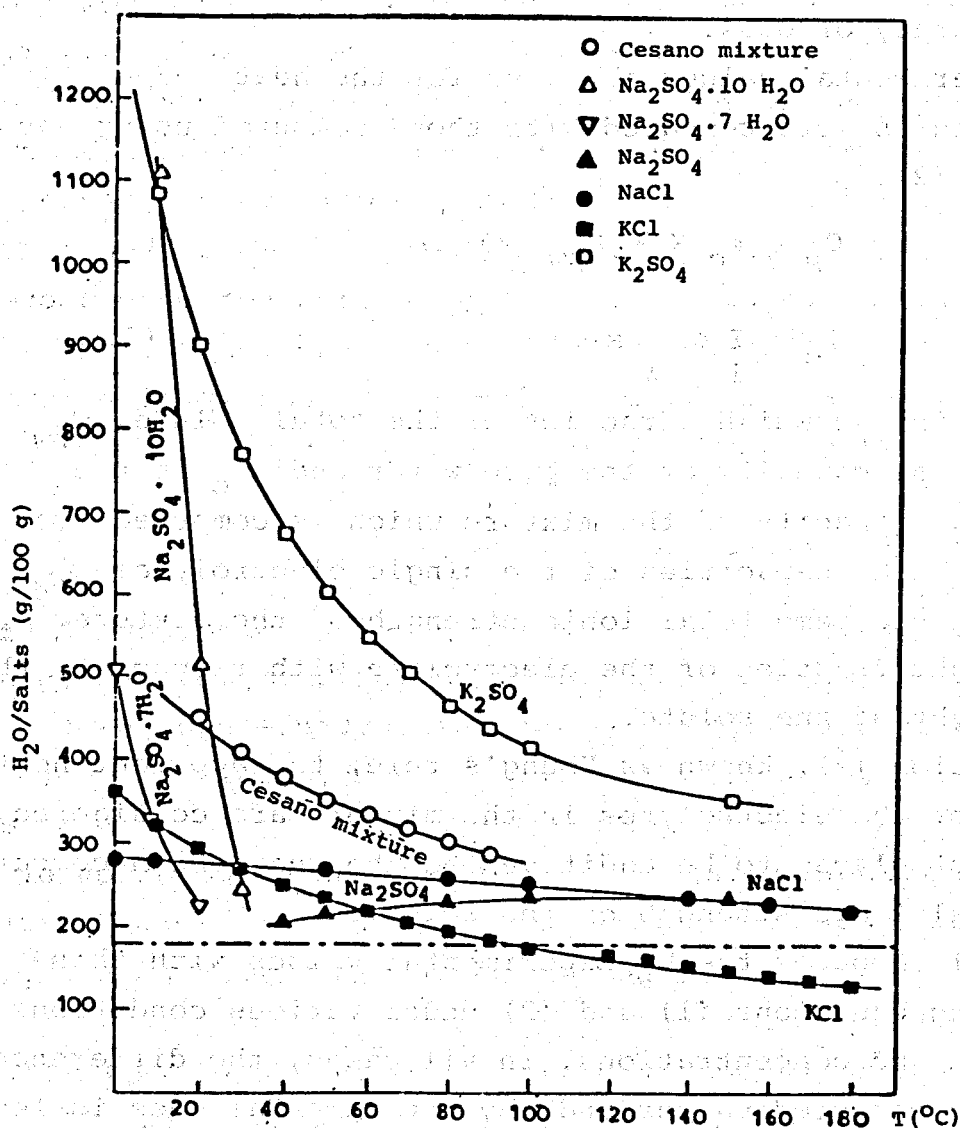


Fig. 5. Integral solubility of pure sodium and potassium chlorides and sulfates and their mixtures in proportion analogous to Cesano-1 brine vs temperature.

centrations and at different ratios between their components. In this study, the heat capacities between 30°C and 80°C have been measured for salt water solutions of NaCl, KCl, Na₂SO₄ and K₂SO₄ and for some of their mixtures for different component ratios and using a CALVET type calorimeter and the "continuous heating" method. The range of temperatures and concentrations studied was limited both by the fact that it was impossible to agitate the mixture while measurements were being made and by other special characteristics of the experimental apparatus. The heat capacities were measured within an estimated accuracy of 0.5%.

The experimental values obtained for the heat capacities of the mixtures were compared with those computed using equations (1) and (2).

$$C_p = \phi_c X + C_{pw} (1-X) \quad (1)$$

$$\phi_c = \sum_i \phi_{c_i} x_i \quad (2)$$

where X is the weight fraction of the total solute, C_{pw} is the heat capacity of the pure water and ϕ_c is the apparent heat capacity of the mixture which is computed from the apparent heat capacities of the single electrolytes ϕ_{c_i} measured at the same total ionic strength of the mixture. x_i is the weight fraction of the electrolyte with respect to the total weight of the solute.

In equation (2), known as Young's rule, the apparent heat capacities of the electrolytes in the mixture are considered, in the first place, to be additives as they have been computed for the total ionic strength of the solution.

Table II compares the C_p experimental values with those computed using equations (1) and (2) under various conditions of temperature and concentrations. In all cases, the difference between the computed values and the experimental ones is less than 1%. We now plan to check the validity of Young's rule for higher concentrations and temperatures and to eventually attempt other correlations. In order to be able to extend the measurements to

TABLE II

Comparison between experimental C_p values and those calculated following Young's rule for selected binary mixtures.

1 a): Temperature dependence at selected ionic strengths I ($I = 1/2 \sum m_i z_i^2$)

NaCl/KCl = 1/1 at $I = 4$			Na ₂ SO ₄ /K ₂ SO ₄ = 1/3 (Glaserite) at $I = 1.5$			NaCl/K ₂ SO ₄ = 2/1 at $I = 1$		
T ^o C	C _p (calc.)	C _p (exp.)	T ^o C	C _p (calc.)	C _p (exp.)	T ^o C	C _p (calc.)	C _p (exp.)
30	0.7819	0.7817	30	0.9109	0.9124	30	0.9347	0.9366
40	0.7835	0.7835	40	0.9135	0.9140	40	0.9363	0.9379
50	0.7851	0.7842	50	0.9158	0.9159	50	0.9378	0.9390
60	0.7864	0.7840	60	0.9179	0.9178	60	0.9391	0.9402
70	0.7873	0.7832	70	0.9196	0.9197	70	0.9406	0.9416
80	0.7880	0.7820	80	0.9213	0.9216	80	0.9422	0.9435

1 b): Concentration dependence at Fixed Temperatures $T = 50^{\circ}\text{C}$

NaCl/KCl = 1/1				Na ₂ SO ₄ /K ₂ SO ₄ = 1/3 (Glaserite)				NaCl/K ₂ SO ₄ = 2/1			
I	Weight %	C _p (calc.)	C _p (exp.)	I	Weight %	C _p (calc.)	C _p (exp.)	I	Weight %	C _p (calc.)	C _p (exp.)
1.0	6.24	0.9275	0.9254	0.6	3.22	0.9626	0.9608	0.33	1.90	0.9759	0.9767
2.0	11.74	0.8700	0.8671	0.9	4.75	0.9470	0.9452	0.67	3.74	0.9561	0.9574
3.0	16.63	0.8231	0.8208	1.2	6.23	0.9315	0.9303	1.00	5.50	0.9378	0.9390
4.0	21.01	0.7851	0.7842	1.5	7.67	0.9158	0.9159	1.33	7.21	0.9196	0.9214

a wider range of temperatures and concentrations, a calorimeter has been constructed and tested to measure the thermal capacity of salt water solutions in the temperature range 50°-250°C and at the relative equilibrium pressures. The sample can be agitated while measurements are being made and saturated solutions in the lower temperature range can, thus, also be analysed. The calorimeter is of the drop calorimeter type and is illustrated in the diagram in Fig.6. The cell of the calorimeter is composed of a cylindrical container in stainless steel with the internal walls completely lined with gold at 1000/1000. The capacity of the cylinder is - 5 cm³. This apparatus makes it possible to obtain the mean heat capacity of the cell and its content between the furnace temperature T_i and the temperature T_f of an underlying calorimeter C , of adiabatic type, where the cell has been dropped.

The ratio between the heat capacity of the cell and the calorimeter is approximately 1:50. If, in a series of experiments at various temperatures, T_i , the values of T_f vary little from a mean value \bar{T}_f , it can be demonstrated that the heat capacity C_T at a temperature T , within the range of the analysed temperatures, can be computed from the following expression:

$$C_T = \bar{C}_T + (T - \bar{T}_f) \frac{d \bar{C}_T}{d T} \quad (3)$$

The values of \bar{C}_T and of the derivative $\frac{d \bar{C}_T}{d T}$ are obtained from a best fitting of the values \bar{C}_{T_i} using polynomial equations of the type:

$$\bar{C}_T = \sum_{j=0}^n a_j T^j$$

The following type of expression can thus be obtained for C_T

$$C_T = \sum_{j=0}^n a_j T^j + (T - \bar{T}_f) \sum_{j=0}^n j a_j T^{j-1}$$

- A = Cell releasing device
- Sh = Adiabatic shield
- B_C = Calorimetric aluminium block
- B_F = Furnace aluminium block
- C = Calorimeter
- F = Furnace
- G = Brass tube
- R = Electrical calibration heater
- H_F = Furnace heating
- H_S = Adiabatic shield heating
- I = Thermal insulation
- K = Sample receiver
- M = Motor for sample revolution
- Pt₁, Pt₂ = Platinum resistance thermometers
- QT = Quartz thermometer probe
- S_f = Position of the sample inside the calorimeter
- S_i = Position of the sample inside the furnace
- T = Circulating water thermostat
- TH = Thermocouples

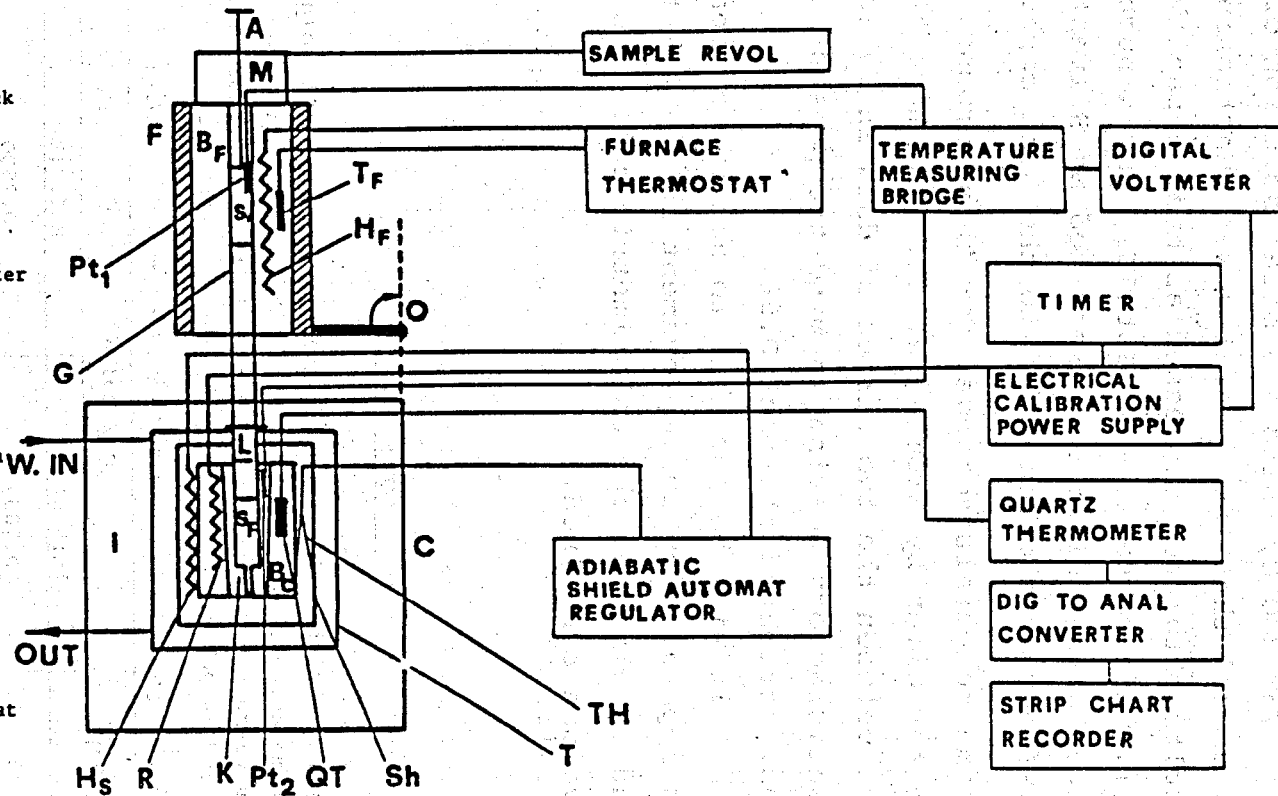


Fig. 6. Scheme of the drop calorimeter.

A first series of experiments has been performed over the temperature range 75°-200°C, using a 6 molal solution of sodium chloride to control that the apparatus was functioning correctly. The results obtained, expressed as heat capacity at constant pressure (C_p), were compared (see Tab.III) for a number of temperature values with similar data reported by Silvester and Pitzer (16). The values given refer to the heat capacity of water in the same temperature range. For this purpose, the values of C_p for water given by Bromley et al. (18) have been used. The agreement between the two series of data in Table III can be considered satisfactory bearing in mind the present accuracy of our apparatus, estimated at about 0.5%. We believe that it will be possible to achieve a greater precision in this apparatus by an improvement in the treatment of the data and by altering the calorimetric cell in order to increase the volume contained.

TABLE III

Comparison of some heat capacity values of a 6 m NaCl solution measured during this study and the corresponding values taken from Silvester and Pitzer in the temperature range 75°C - 200°C.

T(°C)	$C_p / \text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$	
	This study	Ref. (2)
75	0.7837	0.7800
100	0.7791	0.7776
125	0.7754	0.7715
150	0.7729	0.7644
175	0.7722	0.7614
200	0.7766	0.7739

CONCLUSIONS

The initial stage of our experimental research program to study the equilibria and properties of brines has now been completed and we hope to have at our disposal, in the near future, an extensive body of data.

From the results obtained so far it appears unrealistic to think in terms of a theoretical approach; at the present moment, a development in the experimental research methods is necessary if reasonably reliable correlations are to be obtained on the technical level.

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