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Thermodynamics of Natural and Industrial Waters

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The most effective general formulations of thermodynamic equations for multicomponent aqueous solutions are discussed with respect to various ranges of temperature, pressure, and composition with emphasis on solutes important in natural or industrial waters. A familiar equation in molality and in excess Gibbs energy is very successful up to 300°C and ionic strength 6 mol·kg^{-1}, and can often be extended to 350°C or above at high pressure and in favorable cases to ionic strength 12 or even 20. Alternate methods valid to higher solute compositions, even to pure fused salts, are described. A more difficult situation arises near the critical point of water where the compressibility becomes infinite and a Helmholtz energy basis must be adopted. Existing equations for this range and still higher temperatures and pressures are considered and possible improvements discussed.

1. Introduction

Aqueous solutions play a major role in both natural and industrial processes and in waste disposal which is in a sense both industrial and natural. The dominant solutes are often simple electrolytes such as $NaCl$, Na_2SO_4, $CaCl_2$, $MgCl_2$ with lesser amounts of potassium salts, carbonates, borates, etc. While many of these solutions have pH near 7, others may involve simple acids such as HCl or H_2SO_4 or have an excess of OH^-. These solutions are almost always multicomponent mixtures and even though one solute may dominate in quantity, the reactions of minor components may be of great importance. Thus, it is essential to be able to calculate the activity of any component.

While surface and oceanic waters are near room temperature, similar aqueous solutions are present at high temperature in deep geological formations while aqueous systems also arise in steam-power generation and other industrial operations at high temperature and pressure. Thus, there is great practical interest in the thermodynamic properties at these conditions.

From a theoretical viewpoint, electrolytes have been an interesting challenge throughout this century. While Debye and Hückel[1] provided a simple solution to the special problem of an ionic system, further important advances were required to combine correctly the short-range forces with the coulombic interaction and for the

generalization to mixed electrolytes and to higher concentrations.

In this review, I emphasize the recent advances, primarily experimental but including theory, related to high temperature. After a brief reminder of other publications summarizing information near room temperature, I discuss the major progress that has been made in the last two decades for the range 323-573 K. This includes equations for mixtures of unlimited complexity and for concentrations extending to saturation with one or several solids. It is beyond the scope of this paper to present extensive tables of data or of equation parameters, but references to sources of such tables are included. Finally, I discuss briefly the major differences that arise at still higher temperatures and especially as the critical point of water is approached. A few pioneering investigations in this range are listed but are not described in detail.

2. Range 273 - 323 K

Early research on aqueous electrolytes involved rather dilute solutions near room temperature. The data base for pure electrolytes was greatly extended by isopiestic measurements and then masterfully summarized by Robinson and Stokes[2] in their monograph. Harned and his associates[3] investigated many simple mixtures with HCl by electrochemical cell measurements and offered rules for their behavior. Guggenheim[4] improved the original

ion-interaction proposal of Bronsted[5] which offers an excellent base for mixtures, but he claimed validity only to 0.1 $mol \cdot kg^{-1}$. From concepts drawn from recent statistical mechanical treatments, the writer[6,7] was able to propose an improved ion-interaction treatment which represents experimental results to near-experimental accuracy over the full composition range to solid saturation in many cases and to high molalities in other cases. These equations are readily generalized to mixtures[8] of unlimited complexity including neutral as well as ionic solutes (see equation (1) below). The large existing data base was treated on this basis first for single-solute systems[7,9,10] and then for mixtures [8] at moderate concentration.

In 1980 Harvie and Weare[11] used the ion-interaction equations to treat a wide array of natural waters for compositions extending to mineral solubility and demonstrated excellent agreement. Weare and his associates[12,13] extended this work in subsequent years, while Filippov and associates[14-16] independently used the ion-interaction equations in treating many solutions of chemical and metallurgical interest. Both Weare[17] and the writer[18] reviewed the status of this general area for the geochemical community in 1987, and Plummer et al.[19] at the U.S. Geological Survey presented an excellent report accompanied by a computer code. Clegg and Whitfield[20] have presented a very extensive review

for natural waters of various types including the fluid in aerosols as well as ocean, river, and subsurface waters. The situation for aerosols is interesting since the electrolyte becomes more concentrated in air of low humidity; Clegg and Brimblecombe have treated several systems.[21,22]

I will not comment further for this range (273-323K) for strong electrolytes, but do call attention to recent measurements of Hovey, Hepler and associates[23,24] on systems involving substantial ion association. They measured both heat capacities and densities in the range 283-328 K and presented comprehensive treatments of their results and earlier data for several systems. Where there is a reaction at equilibrium, the equilibrium will shift with temperature and the heat of this reaction then yields a contribution to the heat capacity. This can be denoted a "relaxation" heat capacity and designated C^{rel}. Table 1 gives an example excerpted from their extensive tables for $H_2SO_4(aq)$[23] and for the ternary system UO_2SO_4-H_2SO_4-H_2O.[24] It is apparent that the relaxation heat capacity is a very significant contribution in comparison with that for the solute species present $C^{sol\ sp}$.

3. Range 298-573 K

As research is extended upward in temperature, the same general equations and methods are valid in many cases to 573 K or slightly above. The reference pressure must be adjusted from 1 bar = 0.1 MPa to the saturation pressure

or to a higher value in the range above 373 K, of course. A very important experimental study was that of Liu and Lindsay,[25,26] who measured the vapor pressure of aqueous NaCl to 300°C and to the molality of saturation with the solid. They obtained the osmotic coefficients for NaCl over this wide range.

With accurate osmotic-coefficient information established for NaCl as a reference electrolyte for temperatures to 573 K, isopiestic measurements became an efficient method of investigation for other systems. Indeed, Holmes et al.[27] built and tested such equipment, and they have reported numerous measurements extending to 498 K in most cases.[28]

Soon thereafter, two types of flow calorimeters were developed for measurement in this temperature range. For heat capacities a twin, flow calorimeter[29-31] was used for heat capacity measurements for NaCl(aq) to 598 K by Wood and associates[29,30] and for Na_2SO_4(aq) to 473 K by Rogers and Pitzer.[31] Subsequently, similar measurements were made for aqueous solutions of KCl,[32,33] NaBr,[34] NaOH,[35] $MgSO_4$,[36] $MgCl_2$,[37] $CaCl_2$[38] while additional or improved measurements were made for NaCl[39] and Na_2SO_4 (to 573 K).[40] Other systems have been measured to intermediate temperatures, 373 K in many cases.

A second type of calorimetric measurement is that of enthalpy of dilution, and an excellent instrument was developed by Busey et al.,[41] who made very precise

measurements for NaCl(aq) to 573 K (and even to 673 K at the supercritical pressure of 42 MPa). The various measurements, heat capacity, enthalpy of dilution, vapor pressure, etc., are all interrelated thermodynamically. Volumetric measurements are also important for various reasons including their relationship to the pressure dependence of other properties. Since heat capacities and other properties are measured at different pressures, they must be converted to a selected reference pressure for comprehensive correlation. These calculations were carried out for NaCl(aq) by Rogers and Pitzer[42] and by Pitzer, Peiper, and Busey,[43] who also give equations in a form convenient for calculations on the ion-interaction basis.

Table 2 lists many of the aqueous systems for which high-temperature data are available and where a comprehensive treatment was made.[44-50] In most of the comprehensive treatments, ion-interaction equations are developed and temperature-dependent expressions are given for the parameters. The treatments for KCl,[33] Na_2SO_4[40] and $MgSO_4$[36] constitute examples of this type for 1-1, 2-1, and 2-2 electrolytes, respectively. For KCl, Fig. 1 shows the apparent molar heat capacity data[32,33] at several temperatures from 500 to 599 K at 17.9 MPa, with curves calculated from the comprehensive equation. Note that the initial slope as m → 0 is consistent with the Debye-Hückel limiting law, even at 599 K; this indicates

the absence of significant ion pairing. Figure 2 shows a similar comparison with relative apparent molar enthalpies.[51] Similar information for Na_2SO_4 was presented in this journal in my Rossini lecture[52] in 1988. More detailed summaries with equations for the temperature dependence of properties for several electrolytes are available in recent reviews.[18,53,54]

Before considering particular measurements for mixed electrolytes, it is desirable to examine the semi-empirical equations that are in common use. These are the ion interaction (Pitzer) equations.[4,7,18,53] For a mixture of unlimited complexity, the excess Gibbs energy on a molality basis is given by

$$G^{ex}/(w_w RT) = f(I) + 2 \sum_c \sum_a m_c m_a [B_{ca} + (\sum_c m_c z_c) C_{ca}]$$

$$+ \sum_{c>c'} \sum m_c m_{c'} [2\Phi_{cc'} + \sum_a m_a \psi_{cc'a}] + \sum_{a<a'} \sum m_a m_{a'} [2\Phi_{aa'} + \sum_c m_c \psi_{caa'}]$$

$$+ 2 \sum_n \sum_c m_n m_c \lambda_{nc} + 2 \sum_n \sum_a m_n m_a \lambda_{na} + 2 \sum_{n<n'} \sum m_n m_{n'} \lambda_{nn'} + \sum_n m_n^2 \lambda_{nn} + \ldots$$

$$(1)$$

where w_w is the mass of water in kg, $f(I)$ includes the Debye-Hückel limiting law, B_{ca} and C_{ca} are parameters for binary and ternary interactions between ions of opposite sign, $\Phi_{cc'}$ and $\psi_{cc'a}$ involve the differences between interactions of unlike ions of the same sign from the appropriate averages for the like ions cc and c'c' (and similarly for the aa' terms), and finally the terms $\lambda_{nn'}$

λ_{nc}, λ_{na} are for interactions of neutral species with other neutrals, cations, or anions, respectively. All parameters except f(I) are specific to the interacting species and all are functions of temperature. Each B_{ca} is a function of ionic strength as is f(I). In addition $\Phi_{cc'}$ is I dependent if the charges on the ions c and c' are different. Activity coefficients are obtained by appropriate differentiation. The further details are given in many publications including references 7, 8, 11, 18, and 53.

From equation (1) one notes that the B_{ca} and C_{ca} quantities can be obtained from data for pure electrolytes, while the $\Phi_{cc'}$ and $\Psi_{cc'a}$ terms are obtained from data on common ion mixtures of electrolytes ca and c'a. With all terms evaluated, properties of more complex mixtures are predicted. But the Φ and Ψ terms, which arise from differences of interactions, are small and can often be neglected. Indeed Bronsted[5] and Guggenheim[4] assumed that these terms would be zero. We find them to be small but sometimes significant for accurate measurements, and they are well determined for 298 K for the ions of primary interest from isopiestic or electrochemical potential data. Then the calculation of solid solubilities at 298 K requires only the difference in Gibbs energy of formation between the solid and the ions in their standard states. This may be known independently or in any case is only a single quantity

which can be evaluated from a single composition of saturated solution. Then the curves for solubility of that mineral in more complex mixed electrolytes can be predicted. Harvie and Weare[11] and others carried out these calculations for many minerals in equilibrium with various natural waters at 298 K and obtained excellent agreement.

At higher temperatures, the temperature dependency of the pure-electrolyte parameters B and C are now usually known, but in only a few cases are there isopiestic data for mixtures.[55-58] Pabalan and Pitzer[59] considered mineral solubilities at high temperatures and assumed that the more important $\Phi_{cc'}$, $\Phi_{aa'}$ parameters could be taken as constants at their known values for 298 K. Then the smallest and least important parameters $\psi_{cc'a}$, $\psi_{caa'}$ were either omitted or assumed to vary with temperature as $\psi = $ const. $(T^{-1} - 298^{-1})$. This introduced at most one new parameter to be evaluated to fit a large number of solubility values for various temperatures and solution compositions. Figures 3-5 show the results for the ternary systems $NaCl-KCl-H_2O$, $NaCl-Na_2SO_4-H_2O$, and the quaternary $NaCl-KCl-MgCl_2-H_2O$. Note that all parameters for the quaternary had already been evaluated from simpler systems and the comparison in Figure 5 is a strict prediction. Several other systems were considered with similar results in that and subsequent papers.[40,59,60] Moller[49] and Greenberg and Moller[61] have presented

similar treatments for many other minerals, together with convenient equations for pertinent parameters, limited, however, to saturation pressure. Table 3 lists some of the combinations of ions for which the terms ✦ and ✦ are available.

4. Ion Association in the Near-critical and Supercritical Ranges

Although the situation with respect to association of ions into species of lower or zero charge must always be considered, this aspect becomes much more significant in the near-critical range because of the rapid decrease in the relative permittivity (dielectric constant) of water. Usually the pattern of speciation (or status of strong or weak electrolytes) remains the same from 298 K to 523 K and sometimes even to 623 K. But many electrolytes that are treated as fully dissociated at lower temperatures show a clear change in pattern above 523 K. A good example is HCl(aq) as shown on Fig. 6 which displays the enthalpy of dilution data of Holmes et al.[44] A thin straight line shows the Debye-Hückel limiting slope at each temperature and pressure. The experimental measurements from 298 to 525 K are consistent with this limiting slope, but those at 572 K and 32.5 MPa show a clear departure of the type expected for ion association.

The temperature at which ion association becomes significant varies from one electrolyte to another and tends to be lower where the ionic charges are higher. Thus $CaCl_2$ shows[62] a departure like that of HCl but at

523 K, while the heat capacity of KCl[33] shows no departure even at 599 K.

Theory for the ionic association constant yields an equation of the type of

$$\log K_a = f(d_1)\exp(-z_+z_-e^2/d_1 k\epsilon T) \tag{2}$$

where d_1 is the effective distance of closest approach of the two ions. The pre-exponential factor differs slightly for various treatments, but the differences are not important. It is the exponential factor that dominates, with $z_+z_-e^2$ the product of charges and ϵ the relative permittivity or dielectric constant. For SI units the factor $4\pi\epsilon_0$ is inserted before ϵ with ϵ_0 the permittivity of free space. It is the ϵT product that is the primary solvent-related variable and the function $10^5/\epsilon T$ is a convenient basis. The dimension of K^{-1} is omitted hereafter for $10^5/\epsilon T$.

It is found that for $10^5/\epsilon T < 6$ there is little or no association for typical strong electrolytes, while for $10^5/\epsilon T > 16$ association becomes so strong that only a small fraction remains ionized. Figure 7 shows a temperature-density diagram for water with solid lines corresponding to constant values of $10^5/\epsilon T$. Also shown are isobars as dashed curves and the vapor-liquid coexistence curve is dot dashed. One notes that the value of $10^5/\epsilon T$ is determined primarily by density with only a small temperature effect. Thus, the association constant can be correlated almost as well by density as

by $10^5/\epsilon T$. Then one finds for typical strong electrolytes full dissociation for density greater than 0.8 or 0.9 $g \cdot cm^{-3}$ and strong association for density less than about 0.5 $g \cdot cm^{-3}$.

A more detailed picture of association constant behavior is shown on Fig. 8 which gives curves as a function of density for $Na^+ + Cl^-$, $H^+ + Cl^-$, and $NH_4^+ + OH^-$ at 1 kbar (100 MPa) from Mesmer et al.[63,64] For log K_a less than or near zero, association can be ignored in an ion-interaction treatment because a small amount of association at high molality is readily accounted for with the ion-interaction terms -- specifically in B_{ca} which is a function of I.[10] Indeed, the amount of ion association is ambiguous under those conditions in that it is sensitive to the assumed expressions for the activity coefficients of the ions.[65]

In later sections, the information concerning fraction of ion-association will be an important part of the full picture.

5. Reference States and Measurements of Composition for the Near-critical and Supercritical Ranges

The literature[2,3] on electrolytes very generally used molality (moles per kg of solvent) as the measure of composition. This is a very satisfactory quantity provided the amount of water always dominates that of other components. But for an aqueous system miscible to the fused salt, one must instead use the mole fraction because the molality would become infinite for the pure

salt.[60,66,67] For systems with partial ion association or another equilibrium that affects the total number of moles of solute species, however, the use of mole fraction yields much more complex expressions for functions obtained by differentiation.[53,68] The concentration in moles per liter (molarity) has also been used, but it is temperature as well as composition dependent and is less convenient for that reason for thermodynamic purposes.

When the mole fraction is used for an electrolyte, it can be calculated on the dissociated basis counting ions in the totality of moles present if actually dissociated. Alternatively, mole fractions can be calculated on the basis of undissociated solutes regardless of actual dissociation. This is unambiguous for a single electrolyte or for mixtures of the same type of electrolyte, i.e, $NaCl + KNO_3$, but not for more general mixtures. Thus 6 $NaCl$ + $Al_2(SO_4)_3$ with 7 moles might also be regarded as 2 $AlCl_3$ + 3 Na_2SO_4 with 5 moles. There are other objections to the use of an undissociated mole fraction if the system is to be considered at the limit of infinite dilution where it is unquestionably dissociated.

The standard reference state for electrolytes under ambient conditions is that for infinite dilution at the temperature of interest and a pressure of 0.1 MPa (1 bar). For high pressure studies, one uses a reference

state at the pressure of interest instead of 0.1 MPa, and for aqueous systems above 373 K one must use a pressure at least equal to the saturation pressure.

Since heat capacity and enthalpy are related to Gibbs energy as derivatives at constant pressure, it is convenient for a comprehensive evaluation to adopt a reference pressure higher than the saturation pressure at any temperature under consideration. Thus, the reference pressure of 179 bars (17.9 MPa) was adopted for the general study[33] on KCl which extended to 599 K. Many of the measurements were made at that pressure, while other data were adjusted to that pressure by means of volumetric information.

Provided the investigation yields accurate information extending to very low molality and thereby a precise extrapolation to infinite dilution, that type of reference state remains optimum. But where the association equilibrium constant is large, this would require measurements at extreme dilution which are not yet feasible at high temperature. For other reasons, measurements may not extend into the very dilute range but may include the composition of equilibrium with a pure solid. Then the solid is a convenient reference state for that component.

For systems extending to pure liquid salt, the pure liquid is a natural reference state. Also, if the saturation mole fraction of salt is large, even if not

unity, a mole-fraction based equation is convenient with the pure supercooled liquid salt as the reference state.

In summary, while the infinitely dilute reference state is almost universal for electrolyte research near room temperature, for other conditions another reference state is often more convenient and should be chosen. The difference in properties between different reference states is usually known for 298 K and 0.1 MPa and can be transferred to another T and P if the densities and heat capacities are known.

6. Near Critical Region

The compositions and densities of the coexisting vapor and liquid $NaCl-H_2O$ have been thoroughly studied and reviewed[69,70] while much more limited investigations have been reported for $KCl-H_2O$[71] and some other aqueous systems. For $NaCl-H_2O$ the recent measurements of Bischoff and Rosenbauer[72] confirm an early study of Olander and Liander,[73] while some later reports proved to be inaccurate. A table of carefully evaluated densities and compositions is available for $NaCl-H_2O$.[70]

The familiar equation-of-state formulation based on the Gibbs energy as a function of T,P,x is inappropriate near the critical point of the solvent because the compressibility becomes infinite. The detailed nature of the resulting difficulties was discussed by Levelt Sengers et al.[74] The appropriate function for this range is the Helmholtz energy with the independent

variables T, ρ, x. An equation of this type was developed[75] for NaCl-H_2O as an expansion around the critical point of pure H_2O with $(T-T_c)$, $(\rho-\rho_c)$, and x (undissociated) as variables. This equation was reviewed in this journal in my Rossini Lecture;[52] hence, the details are omitted here. It gives a good semi-quantitative representation of the phase compositions over a wide range in temperature to 873 K and in pressure down to that of the three phase equilibrium (solid, liquid, vapor) but does not yield full experimental accuracy. Density data were not used in parameter evaluation and the agreement for densities varies from good for the vapor and near the critical line to poor for the liquid near the three-phase pressure. Thus, there has been progress toward an equation of state for the critical region, but an improved formulation is needed.

The density of water at the critical point is 0.32 $g \cdot cm^{-3}$, which is well into the range for nearly complete association of ions into neutral ion-pair molecules. Thus, dissociation to ions can be ignored in good approximation for the primary equation for the critical region. A separate calculation using K_a can be made for the small fraction ionization if that is of interest.[75] At pressures far above critical, however, dissociation would become substantial and would need to be considered. For this and other reasons, the present near-critical equation has only limited validity at pressures above

that of the vapor-liquid coexistence surface.

7. High Pressure Supercritical Region

There is only very limited information about the properties of $NaCl-H_2O$ and even less for other systems at pressures and temperatures higher than the vapor-liquid coexistence surface. Chou et al.[76] report new measurements and review earlier measurements[77] for the solid salt solubility in both binaries $NaCl-H_2O$ and $KCl-H_2O$ and for the ternary $NaCl-KCl-H_2O$ to 200 MPa and 800 K. For the ternary at the higher temperatures there is extensive solid solubility. Sterner et al.[78] developed Margules-type equations on an undissociated basis for the Gibbs energy and related properties for both the solid solution and the fluid in this system. These equations are valid for all compositions of NaCl and KCl in the anhydrous systems but only at solid saturation for the aqueous fluid.

Another approach, valid for variable compositions below solid saturation in $NaCl-H_2O$, is based on the density measurements of Urusova[79] for the range to 823 K, 100 MPa, and 60 wt %, which give the pressure dependence of the water and salt activities. An equation on a fully dissociated mole fraction basis with a Debye-Hückel term and a single Margules term was developed by Pitzer and Li[80] from this pressure dependency and other information for $NaCl-H_2O$ in range from solid saturation down to a dissociated mole fraction of about 0.2, which

is well above that of the critical line. Figures 9 and
10 compare the activity of H_2O and the chemical potential
of NaCl from this equation (symbols) with curves
calculated from the equation of the previous section
based primarily on vapor-liquid coexistence compositions.
While the agreement is far from perfect, it is good
enough to indicate that both equations are useful for
appropriate ranges. More particularly, the equation
based only on data at lower pressure appears to give
quite good values at 1 kbar. The equation based only on
data at higher mole fractions fails at near-critical
compositions but, interestingly, regains fair accuracy
for very dilute solutions.

Information of a different sort was obtained from
calculations[81] based on a semicontinuum model for ion
hydration. In this treatment, the experimental
measurements by mass spectrometry of inner-shell ion
hydration were combined with the Born equation for
solvation of an ion in a dielectric medium. The
effective ion radius outside of the first hydration shell
and some other details were evaluated from the ion
hydration energies which are known for 298 K and for
somewhat higher temperatures for liquid or liquid-like
densities. Under these conditions the inner hydration
shell is full or nearly full and the sensitive aspect of
the calculation is that for outer-shell parameters. At
higher temperatures and lower solvent density the outer-

shell contribution becomes small and the important variation is that for the inner shell. Thus the mass spectrometric data yield, in effect, predictions for the extended P-T range. In this range there is strong ion association at finite molality and these ionic properties at infinite dilution allow calculation of ion dissociation constants including the self-dissociation of H_2O.[82]

The calculated P-T surfaces for various properties extended to 1273 K and 5 kbar. Figures 11 and 12 show the results for the Gibbs energy and the entropy of hydration, $\Delta_h G/R$ and $\Delta_h S/R$, for various pressures. While $\Delta_h G$ remains finite, $\Delta_h S$ approaches negative infinity at the critical point of water. Estimates of uncertainty were also presented for various P-T regions.

8. Vapor

While the solubility of NaCl and similar salts in steam is very small, it becomes significant near the critical point. This effect is important in steam power engineering since it can deposit a solid on turbine blades. Most of the experimental studies were motivated by this practical need. An equation for NaCl in steam extending to supercritical temperatures was developed by Pitzer and Pabalan[83] and fitted to the available data. There is no significant dissociation to ions in this range. The model was that of successive hydration of the NaCl molecule by one, two, three, etc., molecules of

water. A constant $\Delta_h S$ was assigned on the basis of the mass spectrometric data for ion hydration. Then $\Delta_h H$ values for various stages of hydration were obtained by fitting the solubility data for various temperatures to 873 K and for pressures up to 30 MPa at the highest temperatures. Figure 13 shows the calculated curve and the experimental data for 723 K. The slope indicates hydration by at least 8 H_2O per NaCl at the highest pressure. In the range near 250 bars, the agreement between several investigations leaves little doubt that the one markedly deviant set of data is incorrect. With just two experimental studies at lower pressures, the choice is less obvious. But the vapor pressure of pure NaCl is known and is much more consistent with the lower values of Galobardes et al.[84] than with the higher concentrations of Martynova.[85] Hence, the model was fitted to the lower concentrations.

9. Concluding Remarks

In the range above 323 K but below 573 K, the properties of aqueous electrolytes have been actively investigated in the last two decades and there now good equations which represent the extensive experimental data base and provide good predictions for mixtures as well as pure electrolytes and for molalities up to solid solubility in many cases. At higher temperatures the experimental data base is much more limited and the demands on equations of state are more complex. While there are successful

equations for NaCl-H_2O for certain T,P,x ranges, research is in an early stage both experimentally and theoretically, and there are many opportunities for important advances.

Acknowledgment

Table 1. Equilibrium Speciation, Relaxation Contribution, and Net Solute Species Contributions to Heat Capacity (illustrative values)

m H_2SO_4	UO_2SO_4	α^a	β^a	I	$C_{p,\phi}^{rel.}/R$	$C_{p,\phi}^{sol\ sp}/R$
			H_2SO_4 at 10°C			
1.0127	–	0.3310	–	1.683	18.29	–13.30
0.1035	–	0.3607	–	0.178	14.70	–17.34
			H_2SO_4 at 55°C			
1.0127	–	0.0956	–	1.206	9.67	– 1.84
0.1035	–	0.1233	–	0.129	12.48	– 2.41
			H_2SO_4-UO_2SO_4 at 10°C			
0.6606	0.8725	0.2492	0.9039	1.326	8.83	– 4.51
0.0947	0.0659	0.3300	0.8403	0.199	11.04	–16.09
			H_2SO_4-UO_2SO_4 at 55°C			
0.6606	0.8725	0.0073	0.9625	0.963	5.47	5.68
0.0947	0.0659	0.0676	0.8727	0.141	9.72	1.10

[a] α and β are the fractions associated to HSO_4^- and UO_2SO_4, respectively.

Table 2. Electrolytes for Which Extensive Data and Comprehensive Equations are Available for High Subcritical Temperatures

	Range of		
	T /K	P/MPa	Ref.

1:1 Electrolytes

	T /K	P/MPa	Ref.
HCl	273-648	0-40	44
LiCl	273-523	a	28
NaCl	273-623	0-100	43
NaBr	273-598	0-100	45
NaI	298-373	0-10	46
NaOH	273-623	0-40	35
KCl	273-598	0-50	33
CsF	298-373	0-10	46
CsCl	273-523	0-10	28,46
CsI	298-373	0-10	46

1:2 and 2:1 Electrolytes

	T /K	P/MPa	Ref.
Li_2SO_4	273-498	a	47
Na_2SO_4	273-573	0-20	40
K_2SO_4	273-498	a	47
Cs_2SO_4	273-498	a	47
$MgCl_2$	298-598	0-18	48
$CaCl_2$	298-523	0-10	49
$SrCl_2$	298-473	0-10	50

2:2 Electrolytes

	T /K	P/MPa	Ref.
$MgSO_4$	298-473	0-10	36
$CaSO_4$	298-523	a	49

[a] 1 bar (0.1 MPa) below 373 and P_{sat} above

Table 3. Ions for Which Mixed Electrolyte Properties Are Available for High Subcritical Temperatures

c	c'	anions
Na	K	Cl, SO_4
Na	Mg	Cl
Na	Ca	Cl, SO_4
K	Mg	Cl

a	a'	cations
Cl	SO_4	Na, K, Mg, Ca
Cl	OH	Na
OH	SO_4	Na

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Figure Captions

FIGURE 1.   Apparent molar heat capacities of KCl at 17.9
MPa and several temperatures from 500 to 599 K.   The
solid curves are calculated from the equations and
parameters of Pabalan and Pitzer,[33] whose experimental
values are shown as triangles.   The circles show
experimental values of White et al.,[32] while the dashed
lines show the Debye-Hückel limiting slopes.

FIGURE 2. Calculated relative apparent molar enthalpies
of KCl at 373, 423, and 473 K compared with experimental
values of Mayrath and Wood.[51]

FIGURE 3.   Comparison of calculated and experimental
solid solubilities in the system $NaCl-KCl-H_2O$ from
Pabalan and Pitzer.[59]

FIGURE 4.   Comparison of calculated and experimental
solubilities of Na_2SO_4 in the mixed fluid $NaCl-Na_2SO_4-H_2O$
from Pabalan and Pitzer.[40]

FIGURE 5. Comparison of experimental solubilities with
predicted curves for the system $NaCl-KCl-MgCl_2-H_2O$ from
Pabalan and Pitzer.[59]

FIGURE 6.   The enthalpy of dilution of HCl(aq) from
Holmes et al.[44]   The thin lines marked DHLL show the
Debye-Hückel limiting law.

FIGURE 7. Properties of supercritical H_2O related to ion
association. The solid lines are for constant values of
$(10^5/\epsilon T)/K^{-1}$, while the dashed lines show isobars.

FIGURE 8. The association constants for $Na^{+}+Cl^{-}$ = NaCl, $H^{+}+Cl^{-}$ = HCl, $NH_{4}^{+}+OH^{-}$ = $NH_{3}+H_{2}O$ as a function of density at a constant pressure of 100 MPa (1 kbar).

FIGURE 9. The activity of $H_{2}O$ in NaCl solutions along two isobars: 1 kbar and 581 bars, which is the critical pressure at 500°C. The symbols are calculated from the equation of Pitzer and Li,[80] while the curves are from the equation of Tanger and Pitzer.[75]

FIGURE 10. The chemical potential of NaCl in aqueous solution at 500°C and two pressures. Details as in Figure 9.

FIGURE 11. Curves for the Gibbs energy of hydration of $Na^{+}+Cl^{-}$ for the constant pressures shown in bars from the semicontinuum model of Tanger and Pitzer.[81]

FIGURE 12. Curves for the entropy of hydration of $Na^{+}+Cl^{-}$ at the constant pressures shown in bars from the semicontinuum model of Tanger and Pitzer.[81]

FIGURE 13. Solubility of NaCl in steam at 723 K. The curve is calculated from the equation of reference 82, which also discusses the experimental values and gives detailed citations.
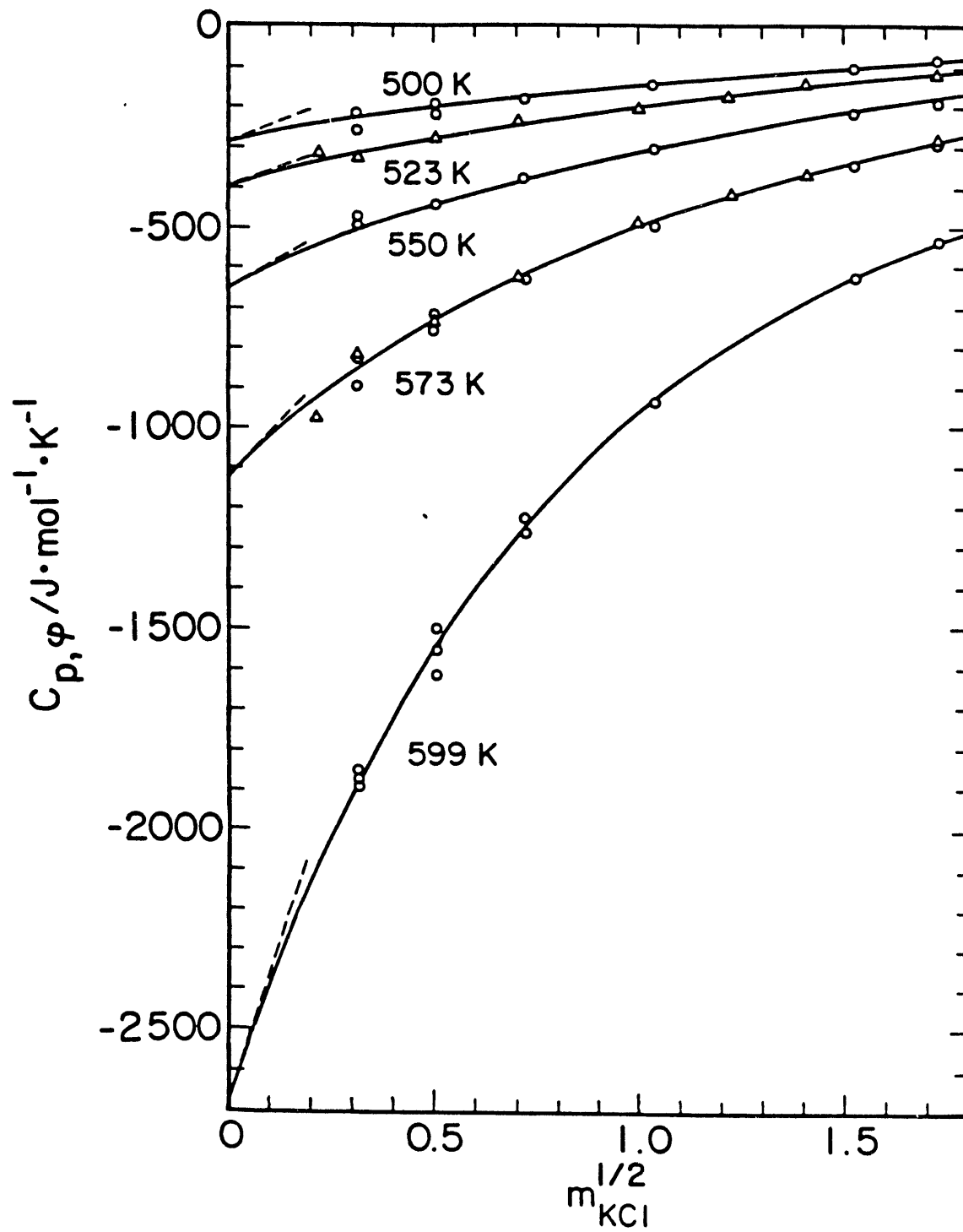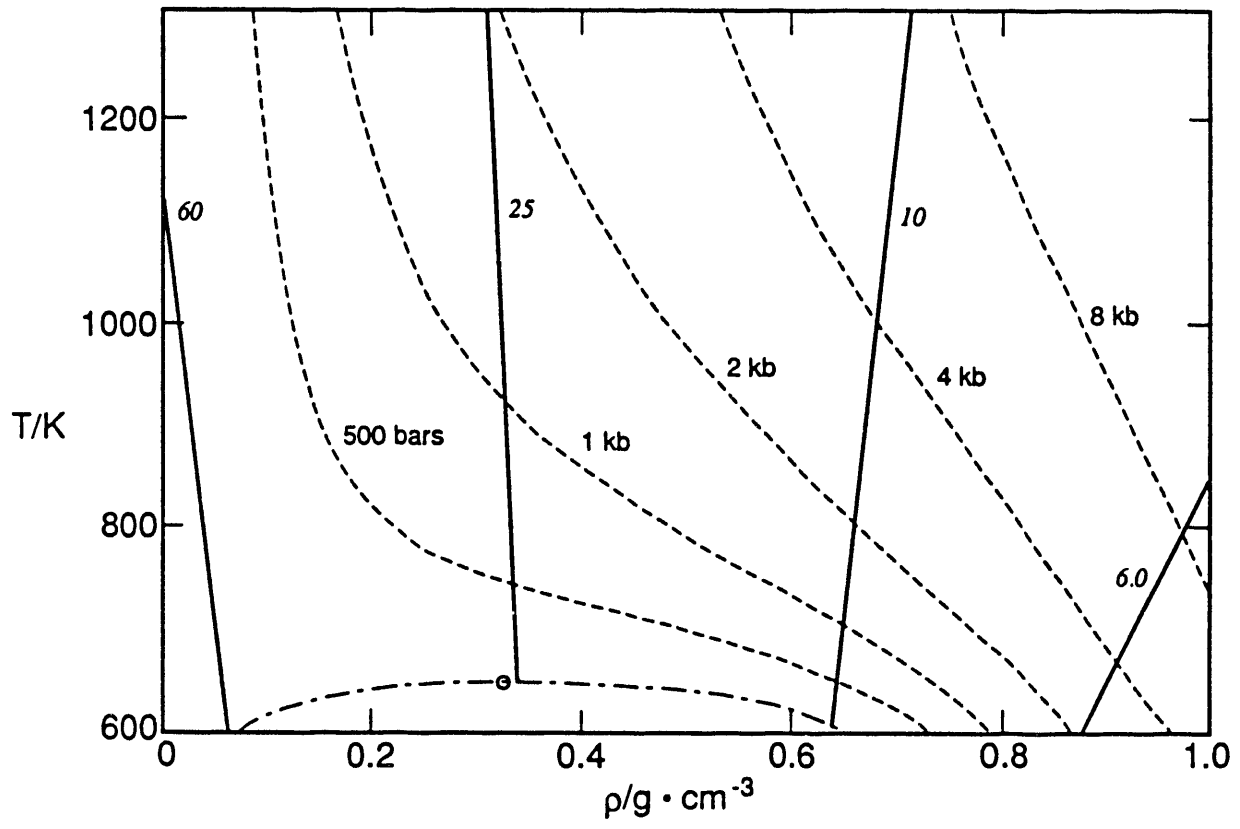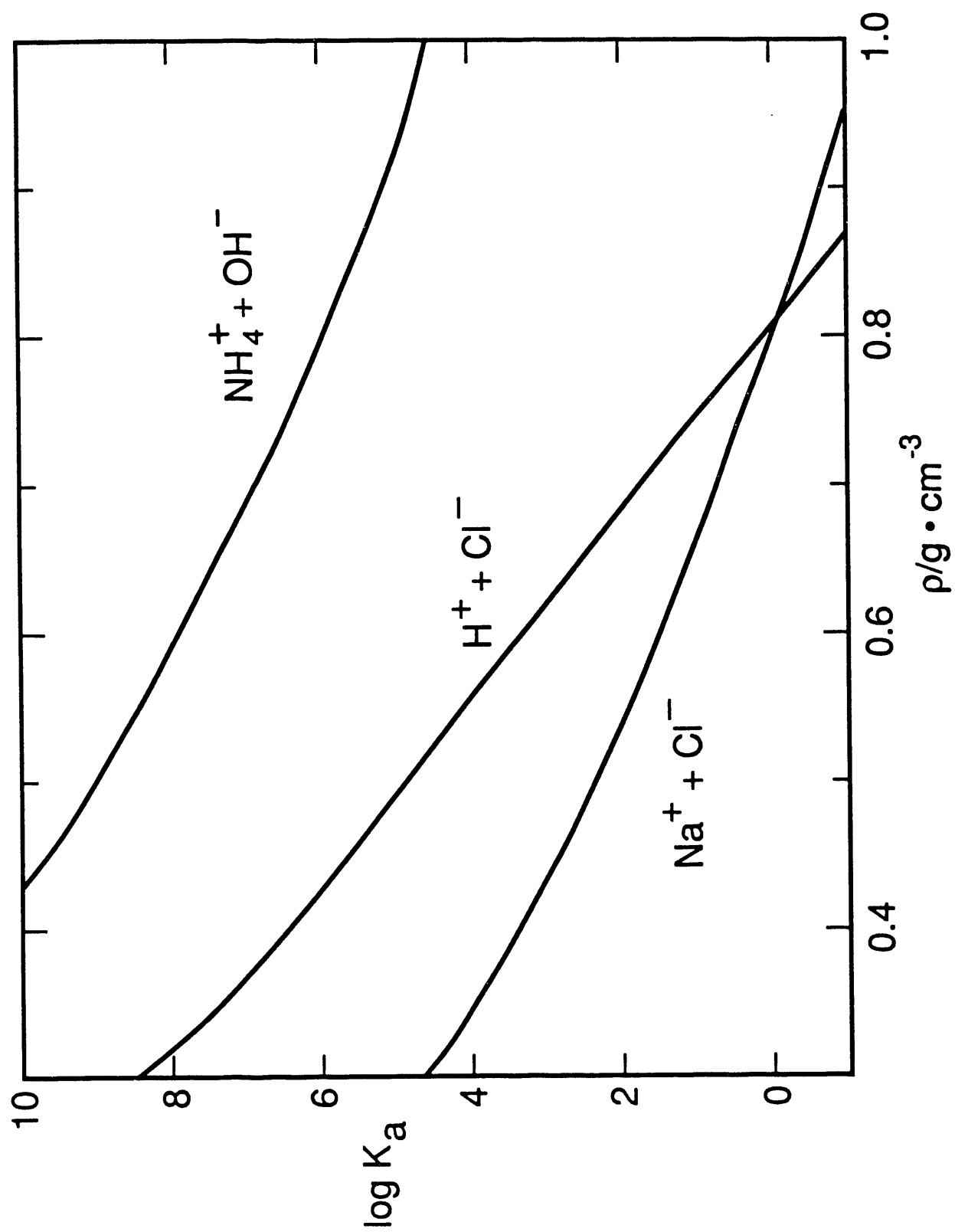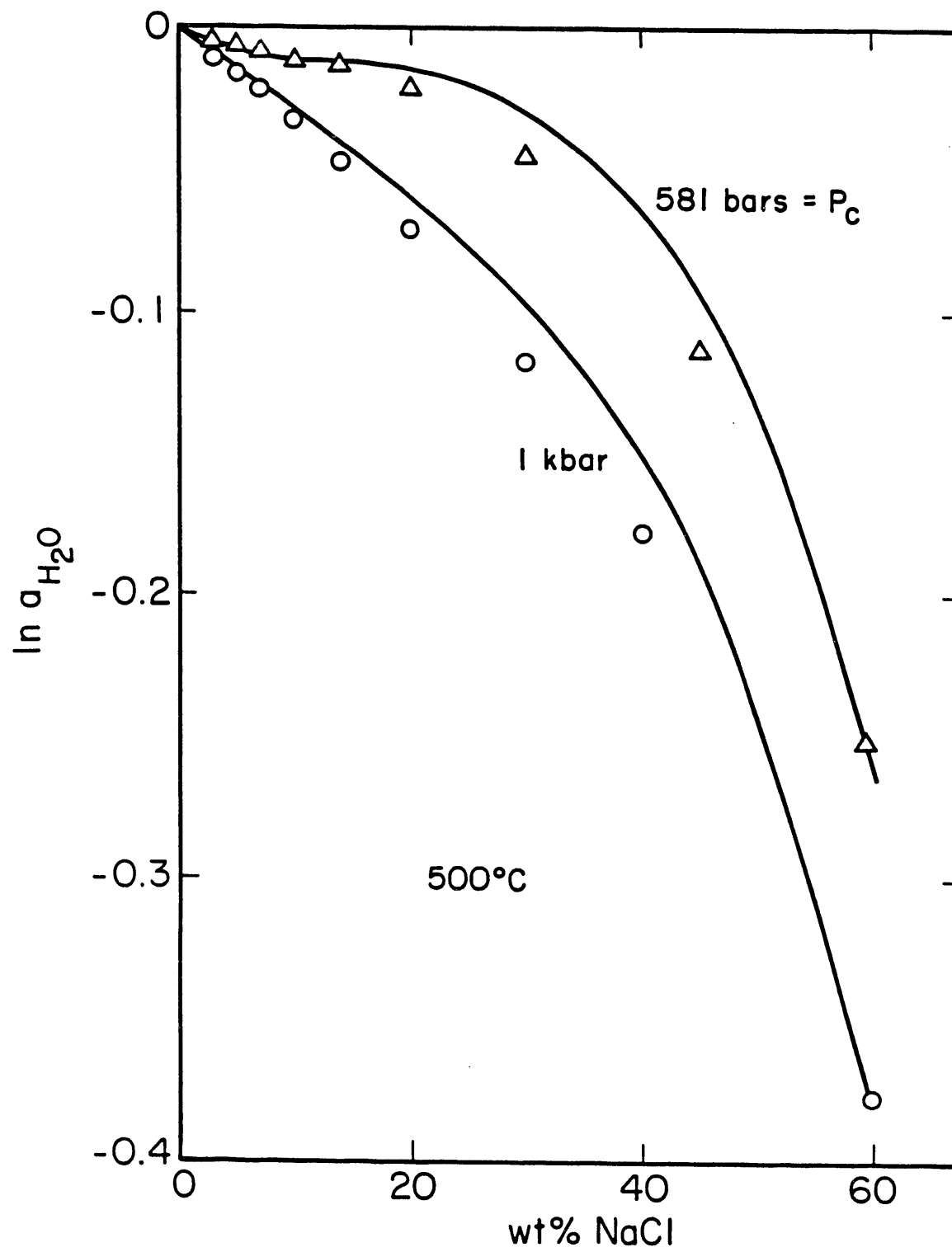
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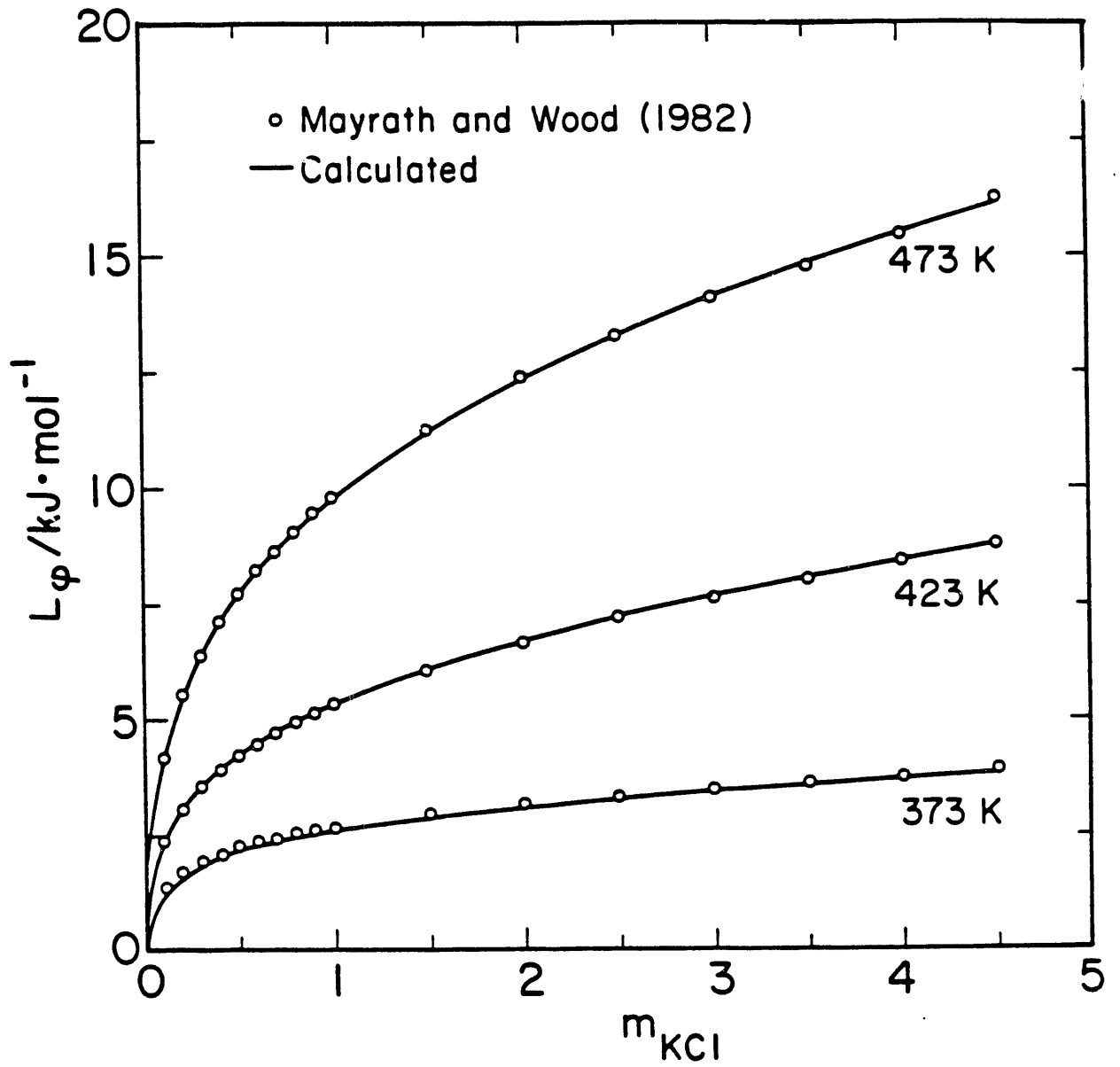
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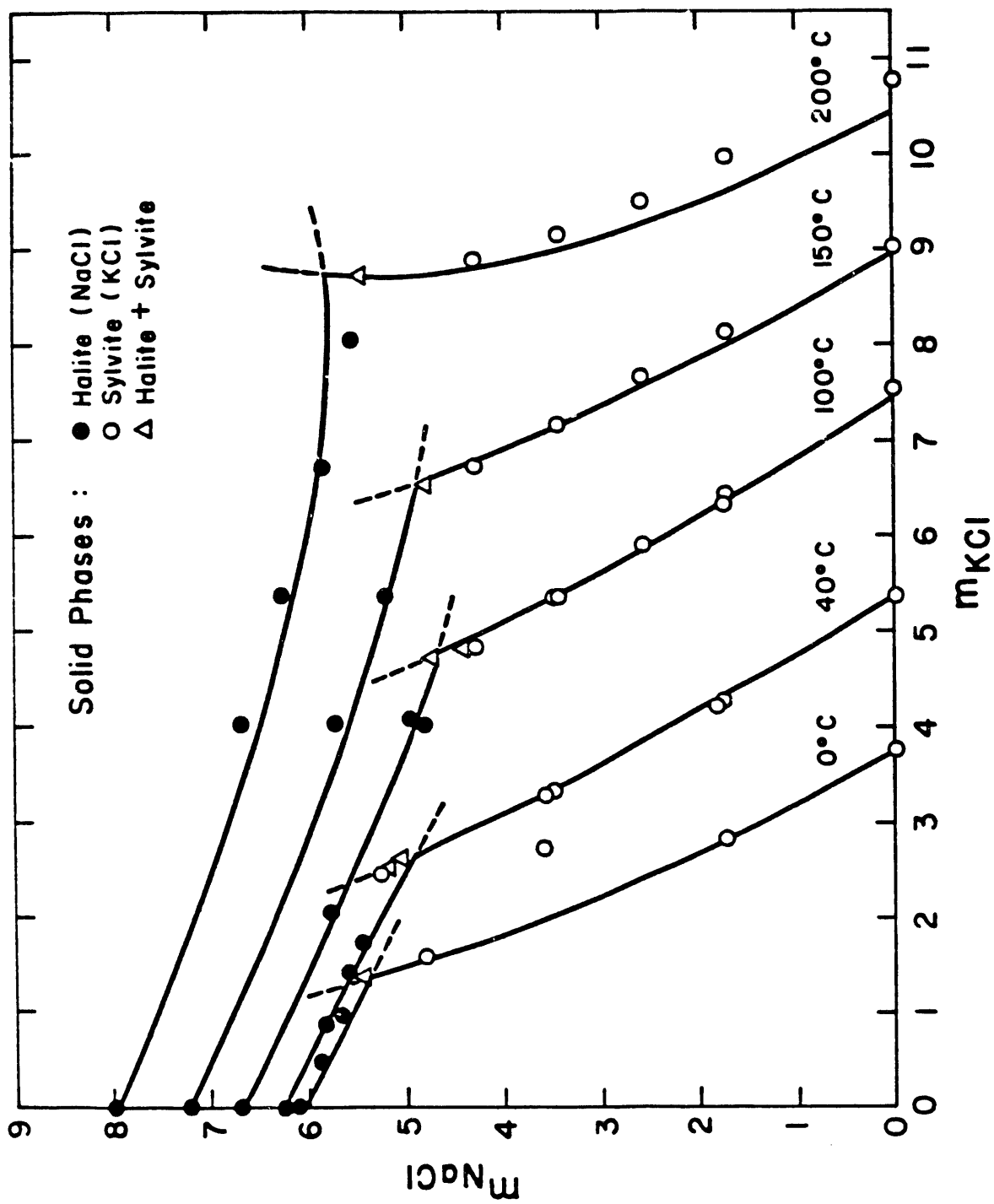
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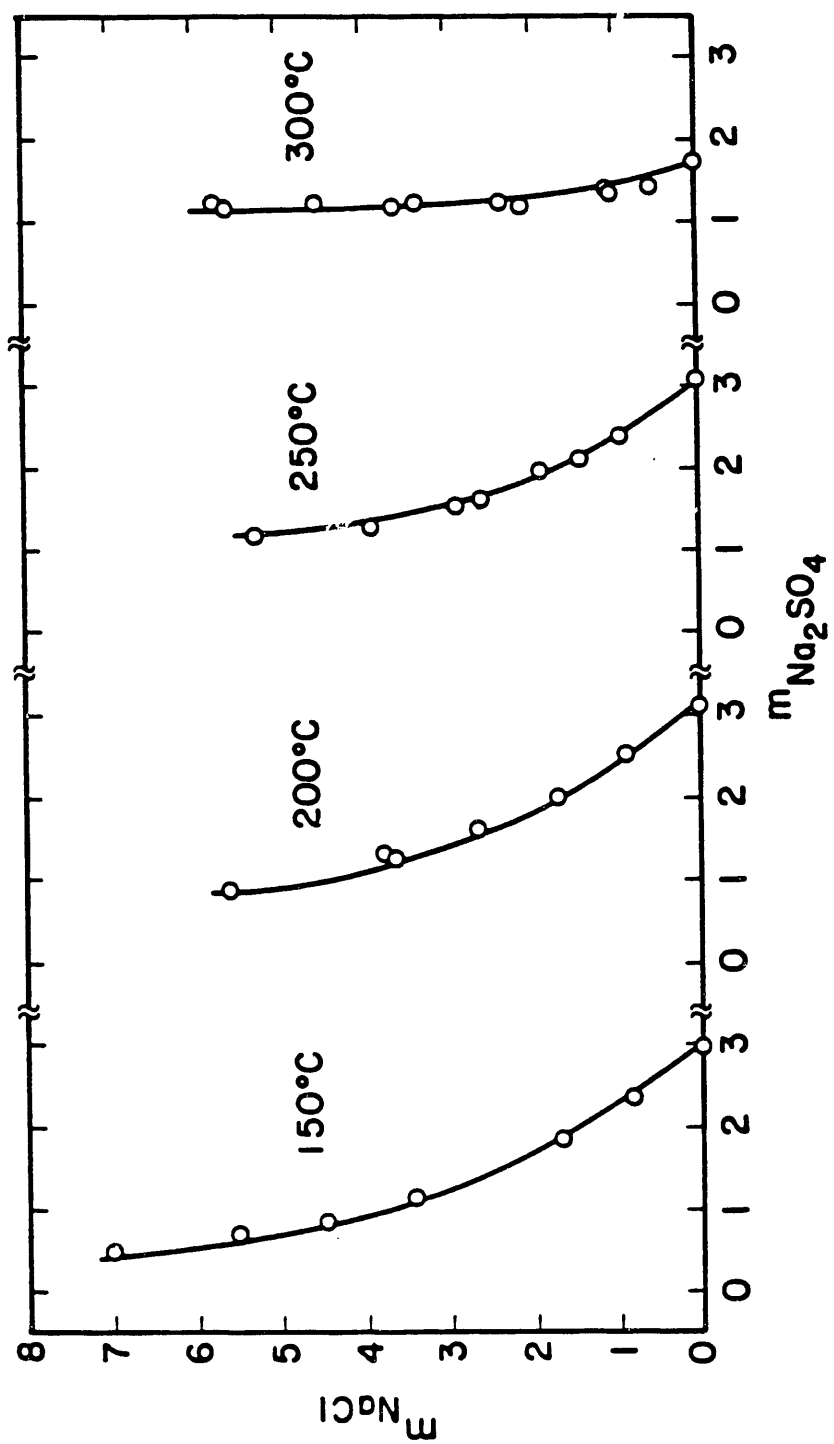
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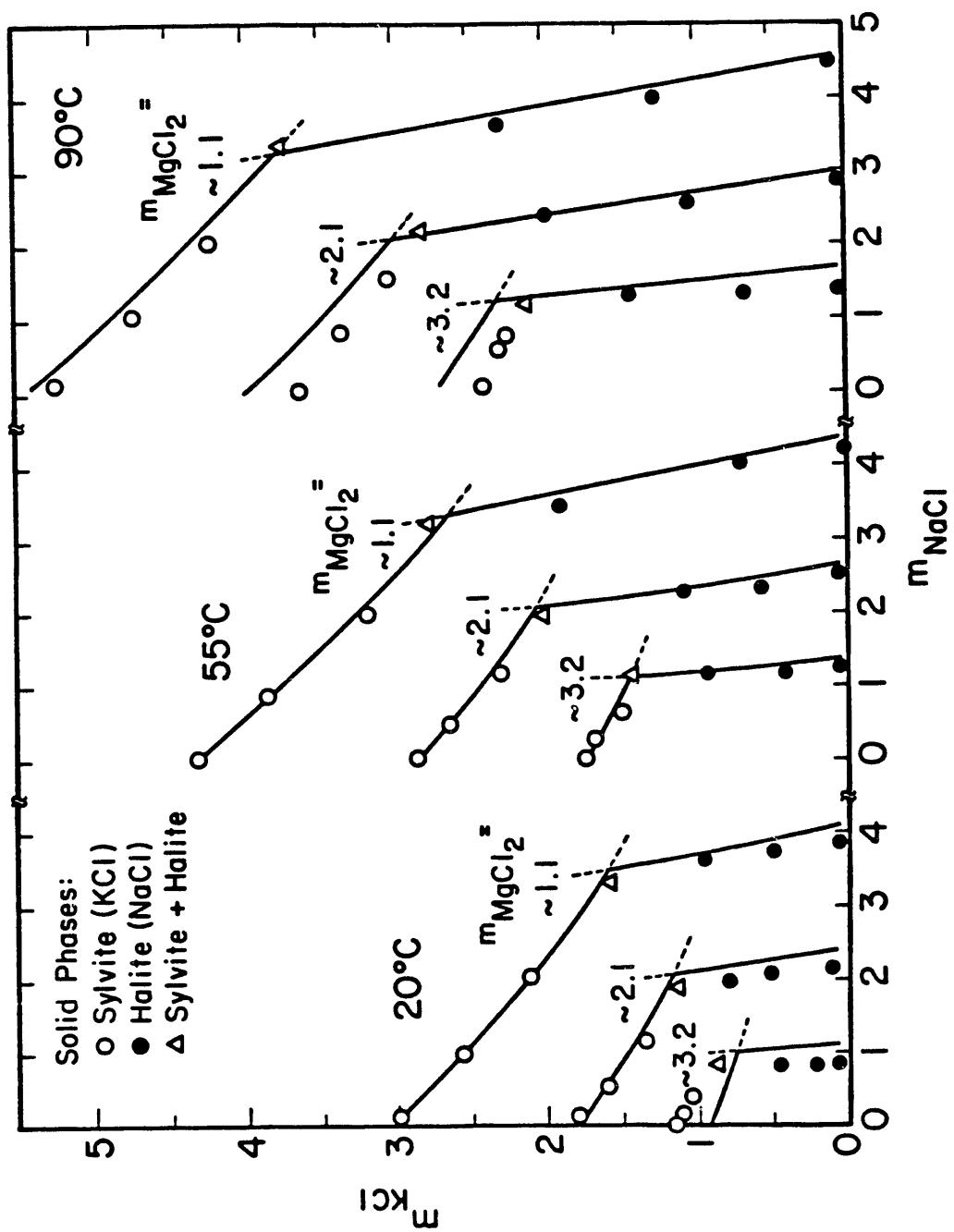
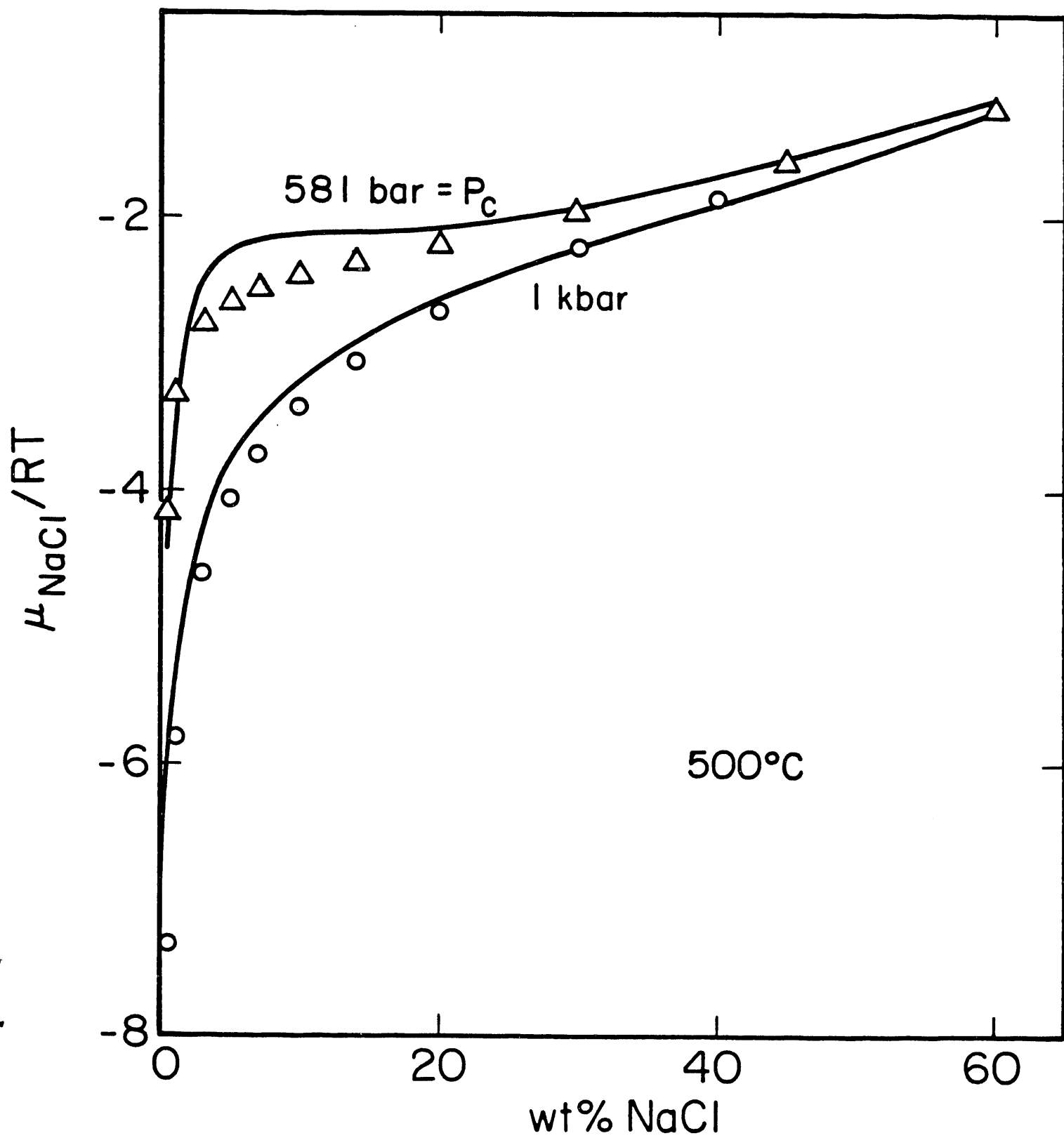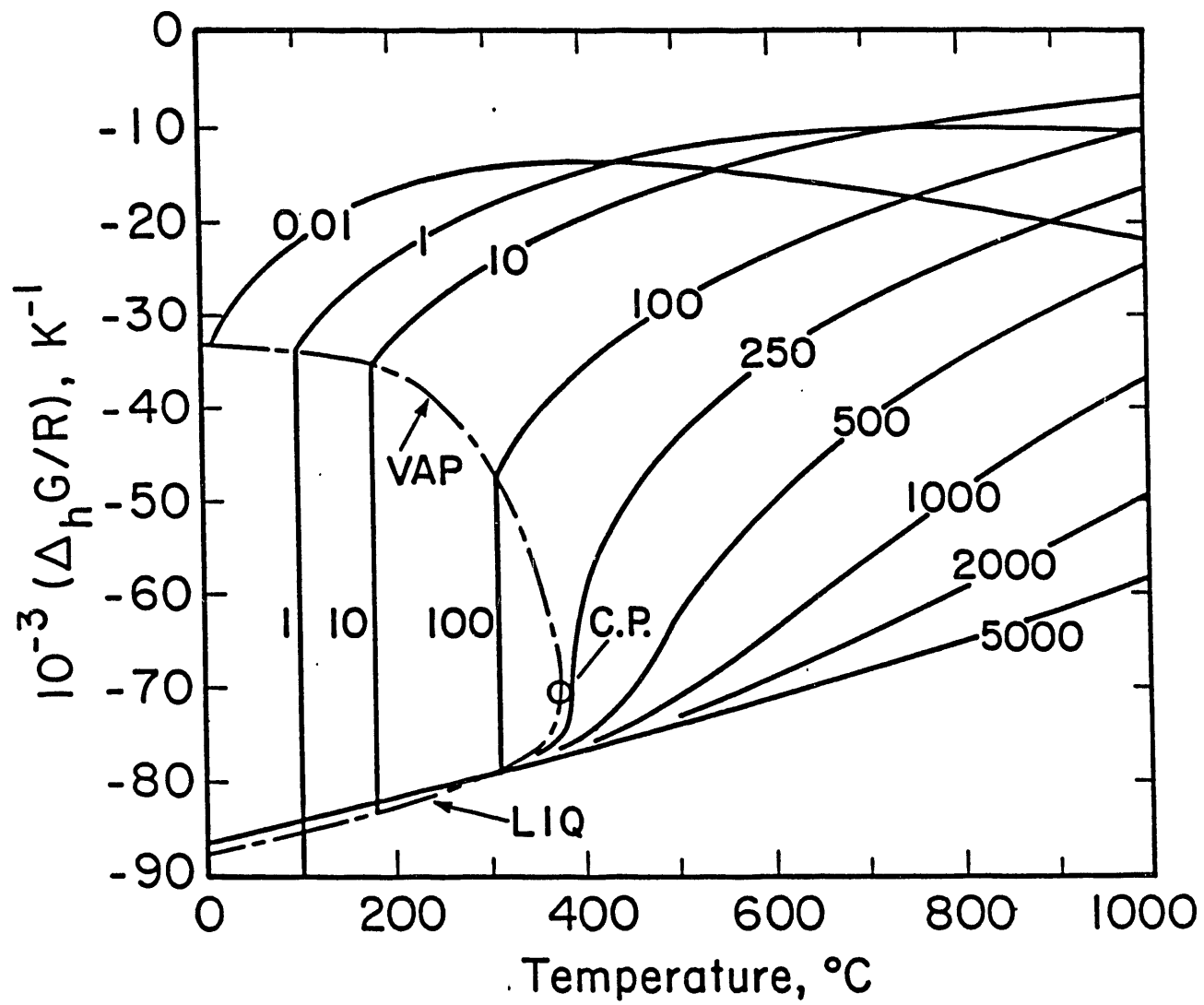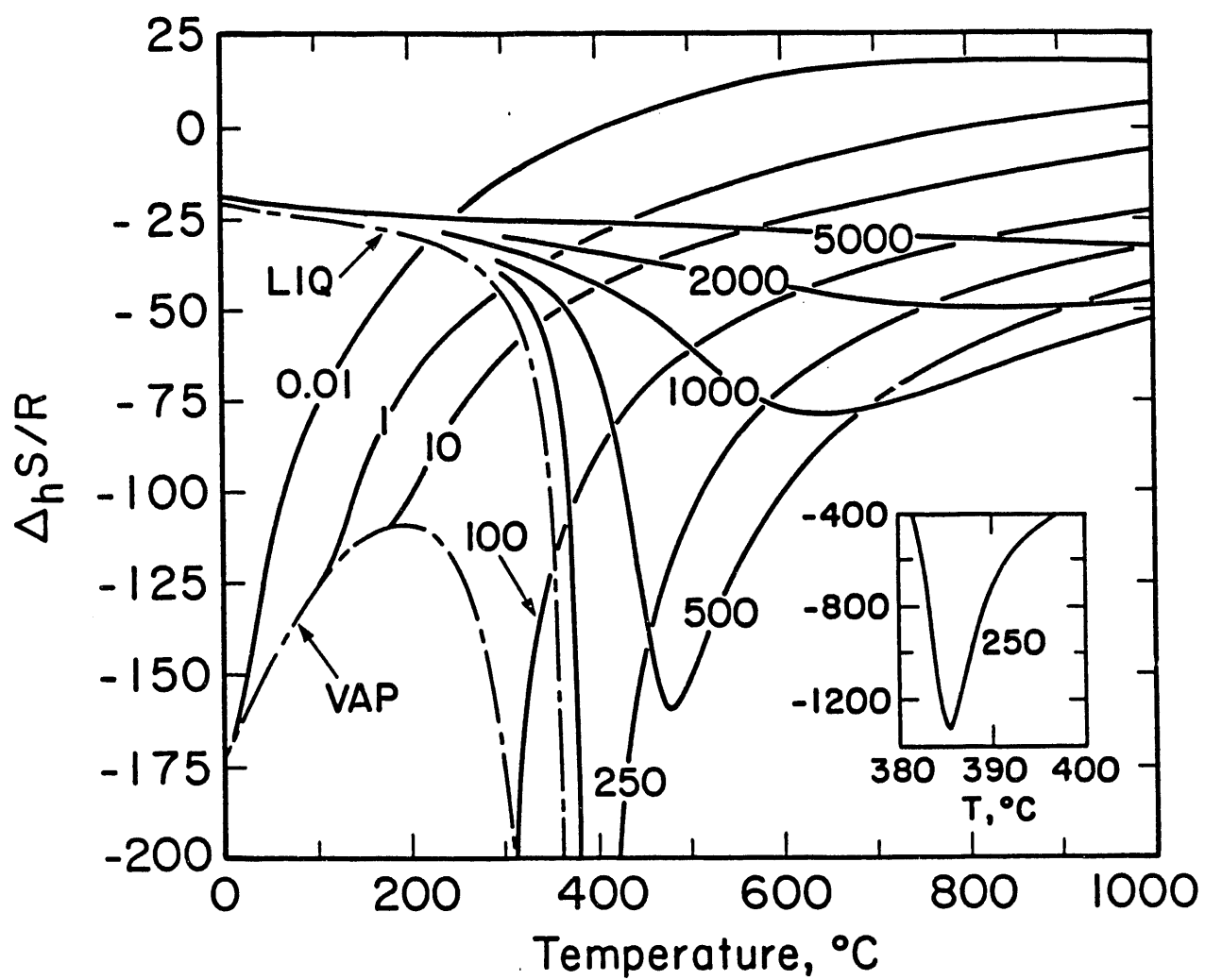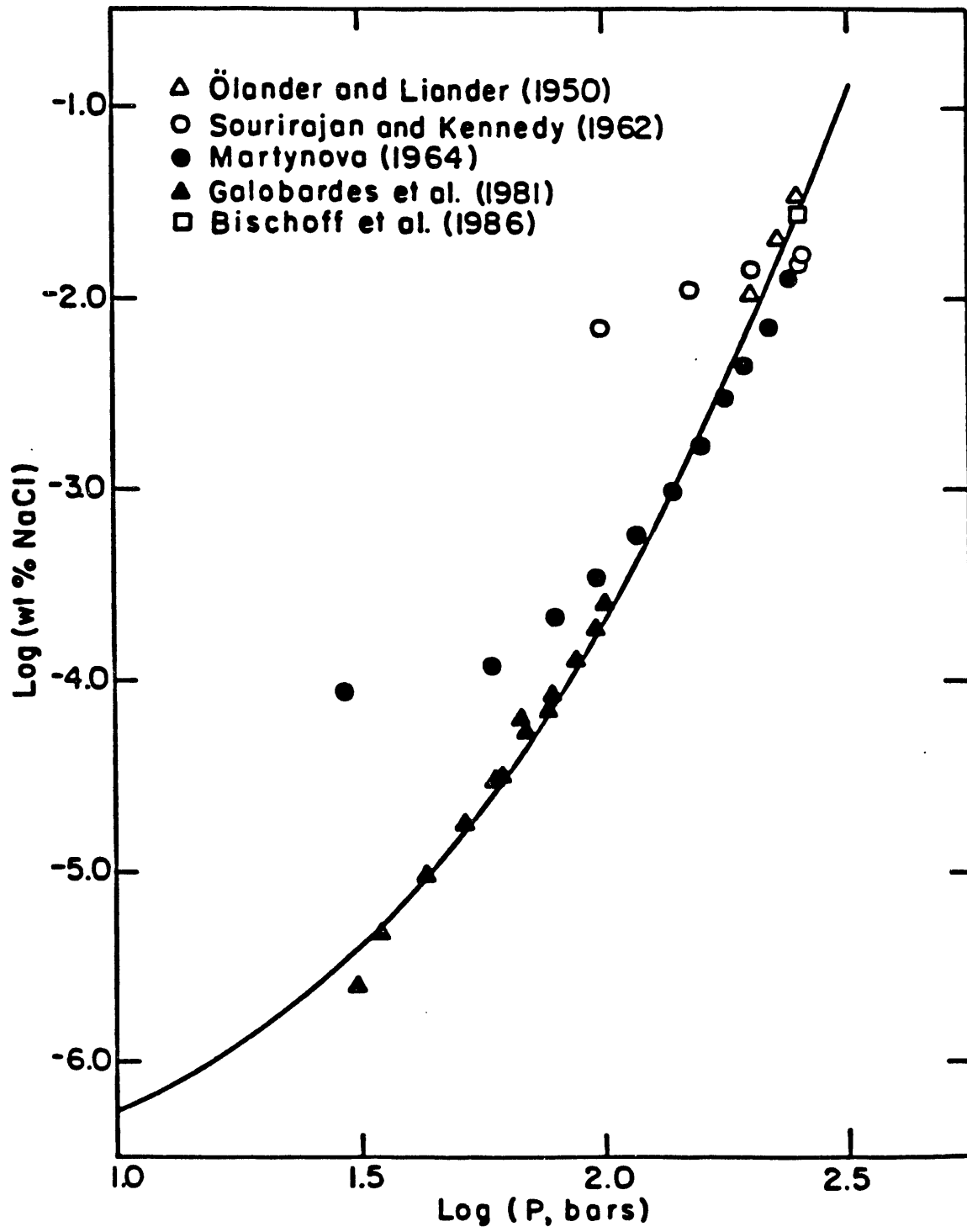Fig. 5
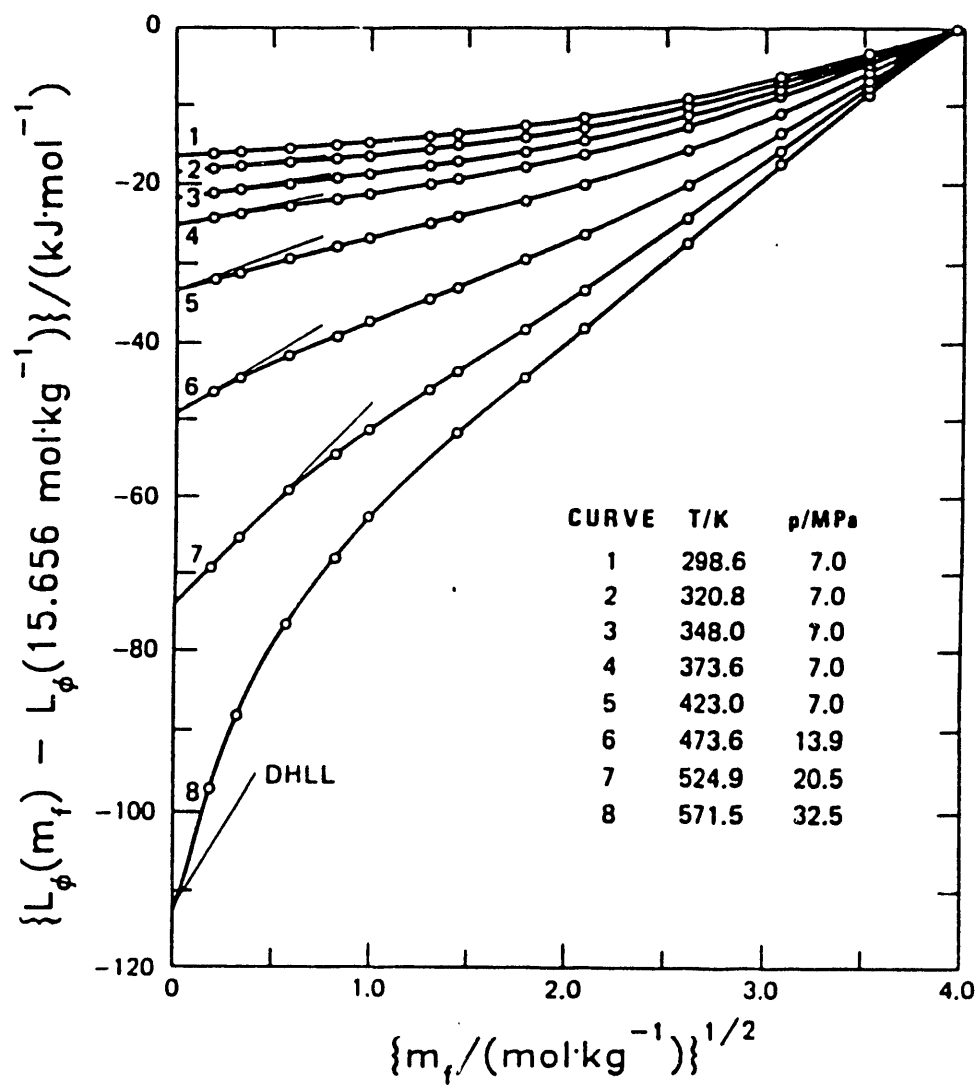
Fig. 6

Fig. 7

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Fig. 10

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Fig. 12

Fig. 13

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