Entropy and Enthalpy Changes for Some Liquid to Vapor Transitions in the System NaCl–H_2O at Supercritical Temperatures

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Values of ΔS and ΔH have been estimated for the following two isothermal, isobaric processes at supercritical temperatures: (I) the vaporization of a saturated liquid solution of NaCl in water to give a vapor solution and solid salt; (II) the transfer of NaCl and H_2O, in a mole ratio corresponding to the mole ratio in the equilibrium vapor solution from an infinite amount of undersaturated liquid solution to the vapor solution. ΔH for process II is, practically, a measure of the heat input required to vaporize at constant temperature and pressure a small fraction of an undersaturated liquid solution. For process I, ΔS and ΔH in the temperature range 385° to 396° C. are of the order of 7 ± 0.3 cal./mole °K. and 4.5 ± 0.3 kcal./mole, respectively. For process II, at 390° C. and for compositions of the liquid solution from approximately 15 weight % NaCl and saturation, ΔS and ΔH increase from about 5.4 to 7.9 kcal./mole °K. and from 3.6 to 5.2 kcal./mole, respectively.

THERE ARE very few data available on high temperature–high pressure, two-component systems and generally what is available is insufficient to calculate thermodynamic quantities such as ΔH or ΔS. In the case of the supercritical NaCl–H_2O systems, we have in the past decade managed to accumulate enough data to make the first such calculations.

On the basis of existing PVT and composition data for the system NaCl–H_2O at supercritical temperatures (*7, 3*), it is possible to estimate ΔS and ΔH at constant temperature and pressure for the following processes

$$1\text{ mole }H_2O + \frac{X_2''}{X_1''}\text{ mole NaCl} \quad \text{(both in saturated liquid solution)}$$

$$\rightarrow 1\text{ mole }H_2O + \frac{X_2'}{X_1'}\text{ mole NaCl} \quad \text{(both in vapor solution)}$$

$$+\left(\frac{X_2''}{X_1''} - \frac{X_2'}{X_1'}\right)\text{ mole NaCl(c)} \qquad \text{(I)}$$

$$1\text{ mole }H_2O + \frac{X_2'}{X_1'}\text{ mole NaCl} \rightarrow 1\text{ mole }H_2O + \frac{X_2'}{X_1'}\text{ mole NaCl} \qquad \text{(II)}$$

(both in an infinite amount of unsaturated liquid solution) (both in vapor solution)

where X is mole fraction, superscripts $'$ and $''$ refer to vapor and liquid phases, respectively, and subscripts 1 and 2 refer to H_2O and NaCl, respectively.

In process I, ΔH is a measure of the heat input required to produce, at constant temperature and pressure from saturated liquid salt solution, a solid salt and a vapor solution of very low composition in salt. ΔH for process II is a differential heat of vaporization and is, practically, a measure, at constant temperature and pressure, of the heat input required to produce a small amount of vapor from a large amount of undersaturated liquid solution. The values of ΔS and ΔH for both processes are of considerable interest in connection with the distillation of salt-water solutions at supercritical temperatures.

To evaluate the entropy and enthalpy changes associated with process I, $\Delta S(\text{I})$ and $\Delta H(\text{I})$, we begin with the coexistence equations for the three-phase equilibrium system vapor solution-liquid solution-solid salt. These equations may be written

$$(\overline{S}_2' - S_2^0)\mathrm{d}T - (\overline{V}_2' - V_2^0)\mathrm{d}P - \frac{\partial\mu_2'}{\partial X_2'}\,\mathrm{d}X_2' = 0 \tag{1}$$

$$(\overline{S}_2'' - S_2^0)\mathrm{d}T - (\overline{V}_2'' - V_2^0)\mathrm{d}P - \frac{\partial\mu_2''}{\partial X_2''}\,\mathrm{d}X_2'' = 0 \tag{2}$$

$$(\overline{S}_1'' - \overline{S}_1')\mathrm{d}T - (\overline{V}_1'' - \overline{V}_1')\mathrm{d}P - \frac{X_2'}{X_1'}\frac{\partial\mu_2'}{\partial X_2'}\,\mathrm{d}X_2' + \frac{X_2''}{X_1''}\frac{\partial\mu_2''}{\partial X_2''}\,\mathrm{d}X_2'' = 0 \tag{3}$$

where, in addition to the symbols already defined, the superscript 0 refers to solid salt and μ is the chemical potential. We are considering the solid phases to be NaCl(c) and not, for example, a hydrate. In the present state of our knowledge of the system, this assumption seems plausible.

Equation 1 to 3, together with the equation

$$\overline{V}_1 = \frac{V}{n_1} - \frac{X_2}{X_1}\,\overline{V}_2 \tag{4}$$

where V/n_1 is the volume of the appropriate phase which contains 1 mole H_2O, may be solved to give

$$\left(\overline{S}_1' + \frac{X_2'}{X_1'}\,\overline{S}_2'\right) - \left(\overline{S}_1'' + \frac{X_2''}{X_1''}\overline{S}_2''\right) - \left(\frac{X_2'}{X_1'} - \frac{X_2''}{X_1''}\right)S_2^0 = \left[\frac{V'}{n_1'} - \frac{V''}{n_1''} - \left(\frac{X_2'}{X_1'} - \frac{X_2''}{X_1''}\right)V_2^0\right]\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_3 \tag{5}$$

where $(\mathrm{d}P/\mathrm{d}T)_3$ is the temperature coefficient of pressure for the three-phase equilibrium system. The total entropy term of Equation 5 is $\Delta S\,(\mathrm{I})$.

To evaluate $\Delta S\,(\mathrm{I})$ there is required, according to Equation 5, the densities and compositions of the three equilibrium phases and the equilibrium pressures at several temperatures. Because the composition of the equilibrium vapor phase is small in NaCl, V'/n_1' is practically $18/\rho'$, where ρ' is the density, and $[(X_2''/X_1'') - (X_2'/X_1')]$ is, within experimental error, X_2''/X_1''. Table I gives the required data and its source. Table II gives the terms of Equation 5 required for the calculation of $\Delta S\,(\mathrm{I})$, the values of $\Delta S\,(\mathrm{I})$ at 385°, 390°, and 396° C., and the corresponding values of $\Delta H\,(\mathrm{I})$, where $\Delta H\,(\mathrm{I}) = T(^\circ\mathrm{K.})\,\Delta S\,(\mathrm{I})$.

Table I. Temperature, Pressure, Density, and Composition Data for the Three-Phase Equilibrium System Vapor–Liquid–NaCl(c).

Temp., ° C.	P, Atm.	ρ', G./Cc.	ρ'', G./Cc.	X_2'', Mole Fraction
385	151^a	0.070^b	1.08^b	0.203^c
	144^c	0.066^d		
	157^e	0.075^d		
390	157^a	0.073^b	1.08^b	0.206^c
	151^c	0.069^d		
	164^e	0.078^d		
396	165^a	0.076^b	1.09^b	0.210^c
	159^c	0.072^d		
	172^e	0.081^d		

[a] Estimated from corresponding vapor density, ρ', on basis of data from (*5*). [b] Based on data of Fisher (*4*). [c] Based on data of Keevil (*6*). [d] Estimated from corresponding pressure on basis of steam table data (*5*). [e] Based on data of Olander and Liander (*7*).

The discrepancy of 13 atmospheres between the equilibrium pressure for saturated liquid solution reported by Keevil (*6*) and by Ölander and Liander (*7*) appears to be a systematic error and so does not affect the value of $(dP/dT)_3$. Interestingly, the pressure estimated from the density data of Fisher (Table I) are very nearly the mean of the pressures reported by Keevil and by Ölander and Liander. It appears quite reasonable to consider that the values of $\Delta S\,(\mathrm{I})$ and $\Delta H\,(\mathrm{I})$ in Table II represent the extreme spread in these quantities.

In order to calculate the entropy and enthalpy changes corresponding to process II, $\Delta S(\mathrm{II})$, and $\Delta H(\mathrm{II})$, the coexistence equations may be represented by the differences between Equations 1 and 2 (to eliminate the solid phase as an equilibrium phase) and by Equation 3. These equations, together with Equation 4, may be solved to give

$$(S_1' - \bar{S}_1'') + \frac{X_2'}{X_1'}\,(\bar{S}_2' - \bar{S}_2'')$$
$$= \left[\frac{V'}{n_1'} - \frac{V''}{n_1''} - \left(\frac{X_2''}{X_1'} - \frac{X_2''}{X_1''}\right)\bar{V}_2''\right]\left(\frac{\partial P}{\partial T}\right)_{X_2''} \qquad (6)$$

where $(\partial P/\partial T)_{X2''}$ is the temperature coefficient of pressure when the composition of the liquid phase is constant. The total entropy term of Equation 6 is $\Delta S\,(\mathrm{II})$.

The primary difficulty in the evaluation of $\Delta S\,(\mathrm{II})$ arises in connection with the terms $\bar{V}_2''$, the partial molal volume of NaCl in liquid solution, and $(\partial P/\partial T)_{X2''}$ of Equation 6. It appears, at temperatures in the neighborhood of 390° C., that $\bar{V}_2''$ is close to zero at about 25% by weight NaCl ($X_2'' \cong 0.1$) and may increase to perhaps about 25 cc./mole at saturation, approximately 46% by weight NaCl (*2*). In this range, the term in Equation 6 involving $\bar{V}_2''$ can be neglected without serious error. Between 25% by weight NaCl and the critical composition (1 to 2% NaCl) $\bar{V}_2''$ apparently becomes rapidly negative and its values are not known. Between 25% by weight NaCl and saturated liquid solution there is no experimental pressure-composition data. However, at constant temperature, the equation (*1*)

$$\log P = a\,(X_2'' + X_2') + b \qquad (7)$$

represents quite accurately the variation of the equilibrium pressure with composition for the vapor–liquid system up to 25% by weight NaCl in the liquid phase. When the constants a and b of Equation 7 are evaluated on the basis of the lower composition data of Ölander and Liander (*7*) the equilibrium pressure of saturated liquid solution at different temperatures lies between the values reported by Olander and Liander and by Keevil (*6*). If then, it is assumed that Equation 7 is valid in the higher composition range, $(\partial P/\partial T)_{X2''}$ can be readily estimated. For values of X_2'' greater than about 0.05 (~ 15% NaCl), X_2' is neglibible in comparison with X_2''.

Table III gives the estimated values of $\Delta S(\mathrm{II})$ and $\Delta H(\mathrm{II})$ at 390° C. together with the quantities required for their calculation by Equation 6. The pressures given in Table III were calculated by Equation 8 with the constants a and b evaluated by use of the data of Ölander and Liander (*7*). The density, ρ', of the vapor phase is the density of steam corresponding to the appropriate pressure. This seems permissible in view of the very low percentage

Table II. Values of ΔS(I) and ΔH(I) and Terms Required for Their Calculation

Temp., ° C.	V''/n'', Cc./Mole	V'/n_1', Cc./Mole	X_2''/X_1''	(X_2''/X_1'') V_2^0, Cc./Mole	$(\partial P/\partial T)$, Atm./° C.	$\Delta S\,(\mathrm{I})$, Cal./Mole ° C.	$\Delta H\,(\mathrm{I})$, Kcal./Mole
385	30.5^a	257^b	0.255	7^c	1.30^d	7.3	4.8
		273			1.37	8.3	5.5
		240			1.37	7.1	4.7
390	30.7^a	247	0.259	7	1.30	7.0	4.6
		261			1.37	7.9	5.2
		231			1.37	6.8	4.5
396	30.9^a	237	0.266	7	1.30	6.7	4.5
		250			1.37	7.5	5.0
		222			1.37	6.5	4.3

[a] $$\frac{V''}{n_1''} = \frac{18\left(1 + \dfrac{X_2''}{X_1''}\,\dfrac{58.45}{18}\right)}{\rho''}$$

[b] The three values of V'/n_1' are based on the three densities, ρ', given in Table I, and are in the same sequence. [c] Based on the assumption that the density of NaCl(c) is about 2 g./cc. [d] The three values of $\partial P/\partial T$ are in the same sequence as the three pressures in Table I. P is with sufficient accuracy a linear function of T over the temperature range in question.

Table III. ΔS(II) and ΔH(II) at 390° C. When the Liquid Phase Is Undersaturated with NaCl

X_2''	NaCl, Wt. %	P, Atm.	ρ', G./Cc.	V'/n_1', Cc./Mole	V''/n_1'', Cc./Mole	$(dP/dT)_{X_2''}$ Atm./° C.	ΔS(II), Cal./ Mole ° C.	ΔH(II), Kcal./Mole
0.20	44.9	158	0.0735	245	29	1.52	7.9	5.2
0.15	36.4	178	0.0895	201	28.5	1.81	7.5	5.0
0.10	26.5	201	0.113	159	27.5	2.15	6.8	4.5
0.07	19.7	216	0.127	142	28	2.33	6.4	4.2
0.05	14.6	227	0.154	117	29	2.55	5.4 (5.1)[a]	3.6 (3.4)[a]

[a] If $\overline{V}_2'' = -100$ cc./mole at $X_2'' = 0.05$

of NaCl in the vapor phase. The term V''/n_1'', was estimated from a density-composition curve for the equilibrium vapor-liquid system at 390° C. (*3*). It was assumed in the calculation of ΔS(II) and ΔH(II) that $\overline{V}_2'' = 0$. It will be noted in Table III that if $\overline{V}_2''$ is as large in magnitude as -100 cc./mole at $X_2'' = 0.05$, that ΔH(II) is decreased only about 6%. Over most of the composition range given, it seems unlikely that the neglect of $\overline{V}_2''$ produces an error of more than 1 or 2%.

By combining the coexistance equations for the liquid-vapor system we can show that

$$\left(\frac{\partial \mu_2''}{\partial X_2''}\right) = \frac{\left[\frac{V''}{n_1''} - \frac{V'}{n_1'} - \left(\frac{X_2''}{X_1''} - \frac{X_2'}{X_1'}\right)\overline{V}_2''\right]\left(\frac{\partial P}{\partial X_2''}\right)_T}{\left(\frac{X_2''}{X_1''} - \frac{X_2'}{X_1'}\right)} \quad (8)$$

The term $(\partial P/\partial X_2'')_T$ can be obtained by differentiating Equation 7. In the region where $X_2' \ll 1$ it is given by

$$(\partial P/\partial X_2'') = 2.303\,a\,P \quad (9)$$

Tables IV and V list the values of $(\partial \mu_2''/\partial X_2'')$ for the saturated liquid solutions at different temperatures and for the undersaturated liquid phase at 390° C., respectively.

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Table V. Values of $(\partial \mu_2/\partial X_2'')$ for Equilibrium, Unsaturated Liquid Phase at 390° C.

X_2''	P, Atm.	$(\partial P/\partial X_2'')_T$, Atm.	$(\partial \mu_2''/\partial X_2'')$, Kcal./Mole
0.20	158	−382	8.0
0.15	178	−440	10.4
0.10	201	−486	13.9
0.07	211	−510	18.5

Table IV. Value of $(\partial \mu_2''/\partial X_2'')$ for Saturated Liquid Phase

Temp., ° C.	$(\partial P/\partial X_2'')_T$, Atm.	$(\partial \mu_2''/\partial X_2'')$, Kcal./Mole
385	−352	7.8
390	−375	7.9
396	−405	7.9

NOMENCLATURE

ΔS = entropy change (cal./mole ° K.)
ΔH = enthalpy change (Kcal./mole)
X_1', X_1'' = mole fraction of component 1 (subscript) in prime vapor and double prime (liquid) phases
$\overline{S}, \overline{H}, \overline{V}$ = partial molar entropy, enthalpy or volume
S^0, H^0, V^0 = molar entropy, enthalpy or volume of solid phase
μ = chemical potential (cal./mole)
n_i = number of moles of i component
V = volume (cc.)
P = pressure in atmospheres
T = temperature (° K. or ° C. as indicated)
ρ'' = density of double prime phase (g./cc.)

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