Thermodynamics II

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Chap. 12 Solution Thermodynamics : Applications

Chap11 : Fundamental eqn. & definition of solution thermodynamics
Chap12 : 1. VLE data from γ_i correlations
2. mixing experiment (change of thermodynamic properties during mixing)

12.1 Liquid phase properties from VLE data

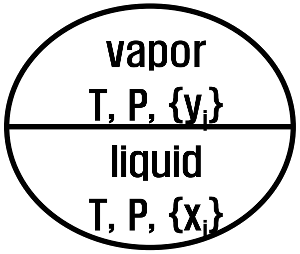

Fig. 12.1 Schematic representation of VLE.

■ Fugacity

For species i in the vapor mixture, Eqn(11.52) $\hat{\phi}_i = \dfrac{\hat{f}_i^l}{y_i P}$

$$\hat{f}_i^v = y_i \hat{\varphi}_i^v P$$

By criterion of VLE $(\hat{f}_i^v = \hat{f}_i^l)$ $\therefore \hat{f}_i^l = y_i \hat{\varphi}_i^v P$

Most of VLE measurement : carried out at low pressure

-> assume to be ideal gas $\hat{\varphi}_i^v = 1$

$\therefore \hat{f}_i^l = \hat{f}_i^v = y_i P$ (fugacity of species i in both liquid & vapor is partial pressure of species i in the vapor phase)

Table 12.1

1st three column, experimental data

Column 4,5 -> $\hat{f}_1 = y_1 P, \hat{f}_2 = y_2 P$

■ Activity Coefficient

Lewis/Randall rule => provide the simplest possible model for the composition dependent of $\hat{f}_i$ => act as a standard to compare actual behavior

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} = \frac{\hat{f}_i}{\hat{f}_i^{id}}$$

$\Rightarrow$ Ratio of actual fugacity to the value from L/R rule at the same, T, P composition

$$\therefore \hat{f}_i = x_i \gamma_i f_i \Rightarrow \qquad x_i \gamma_i f_i = y_i \hat{\varphi}_i P, \quad f_i = \varphi_i^{sat} P_i^{sat} \exp \frac{v_i^l (P - P_i^{sat})}{RT} \qquad (11.44)$$

$$\therefore y_i \hat{\varphi}_i P = x_i \gamma_i \varphi_i^{sat} P_i^{sat} \exp \frac{v_i^l (P - P_i^{sat})}{RT}$$

at low pressure poynting correction ≈1 $\quad \varphi_i = \varphi_i^{sat} = 1$

$$\therefore y_i P = x_i \gamma_i P_i^{sat} \qquad \therefore \gamma_i = \frac{y_i P}{x_i P_i^{sat}}$$

=> Restatement of Eq(10.5) for modified Raoult's law

=> calculation of γ_i from experimental low-pressure LVE data

=> last two columns of Table 12.1

■ Relation between Henry's & Randall rule

※ Dotted line by L/R rule : tangent to $\hat{f}_i$ vs x_i plot

when x_1 -> 1 $\quad \hat{f}_1 = f_1 \quad \therefore (\frac{\hat{f}_1}{x_i} = f_1 \Rightarrow L/R)$

when x_2 -> 0 $\quad \hat{f}_2 \to 0 \quad$ cannot determine $\frac{\hat{f}_i}{x_i}$

=> use l'Hopital's rule

$$\lim_{x_i \to 0} \frac{\hat{f}_i}{x_i} = \left(\frac{d\hat{f}_i}{dx_i}\right)_{x_i=0} \equiv H_i \qquad (12\text{-}2)$$

H_i : limiting slope of the $\hat{f}_i$ vs x_i curve at $x_i = 0$ tangent curve at

$$x_i = 0 \rightarrow \hat{f}_i = x_i H_i$$

■ Henry's law (solubility of gas in liquid)

Mass of gas dissolved in solution ∝ partial pressure of gas above the solution

$$y_i P = x_i H_i$$

$y_i P$: In real gas, replaced by $\hat{f}_i$

- Henry's law only applied when $x_i \to 0$

■ Relation b/w Henry's law & L/R rule

G/D eqn at const T, P $\sum_i x_i d\overline{M}_i = 0$

For binary system, $\overline{M}_i = \overline{G}_i = \mu_1,$ $x_1 d\mu_1 + x_2 d\mu_2 = 0$

$\mu_i = \Gamma_i(T) + RT\ln\hat{f}_i$ (11.46)

At const T , $d\mu_i = RTd\ln\hat{f}_i$ $\therefore x_1 d\ln\hat{f}_1 + x_2 d\ln\hat{f}_2 = 0$

Divide by dx_i $x_1\frac{d\ln\hat{f}_1}{dx_1} + x_2\frac{d\ln\hat{f}_2}{dx_1} = 0$ $, dx_1 = -dx_2$

$$\therefore x_1\frac{d\ln\hat{f}_1}{dx_1} = x_2\frac{d\ln\hat{f}_2}{dx_2} \rightarrow \frac{d\hat{f}_1/dx_1}{\hat{f}_1/x_1} = \frac{d\hat{f}_2/dx_2}{\hat{f}_2/x_2}$$

because $d\ln\hat{f}_1 \Rightarrow \frac{d\hat{f}_1}{\hat{f}_1}$

In the limit $x_1 \rightarrow 1 \quad (x_2 \rightarrow 0)$

$$\lim_{x_1\rightarrow 1}\frac{d\hat{f}_1/dx_1}{\hat{f}_1/x_1} = \lim_{x_2\rightarrow 0}\frac{d\hat{f}_2/dx_2}{\hat{f}_2/x_2} \rightarrow \qquad \frac{1}{f_1}\left(\frac{d\hat{f}_1}{dx_1}\right) = 1$$

$\therefore \left(\frac{d\hat{f}_1}{dx_1}\right)_{x_1=1} = f_1$ => L/R applied to real solution when $x_i \rightarrow 1$

$\therefore$ When $x_i \approx 1$, $\hat{f}_1 \approx \hat{f}_i^{id} = x_i f_i$

Excess Gibbs Energy

From (11.99) $\frac{G^E}{RT} = \sum x_i \ln \gamma_i$ for a binary system, $\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$ (12-6)

$\gamma_i \rightarrow 1$ when $x_i \rightarrow 1$

when $x_i \rightarrow 0$ $\ln \gamma_i \rightarrow \ln \gamma_i^{\infty}$

$\therefore \ln \gamma_i \rightarrow 0$ when $x_i \rightarrow 1$

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (12\text{-}6)$$

$$\left\{ \begin{array}{l} \text{when } x_i \rightarrow 0 \qquad 0 \times \ln \gamma_1^{\infty} + 1 \times \ln 1 = 0 \\ \therefore x_i \rightarrow 0 \qquad \frac{G^E}{RT} = 0, \qquad x_2 \rightarrow 0 \quad \frac{G^E}{RT} = 0 \end{array} \right.$$

$G^E > 0$: positive deviation from Raoult's law, $G^E < 0$: negative

In the case of $\frac{G^E}{x_1 x_2 RT}$, we cannot find the values at $x_1 = x_2 = 0$

Thus for x_1 → 0, use L'Hopital's rule

$$\lim_{x_1 \to 0} \frac{G^E}{x_1 x_2 RT} = \lim_{x_1 \to 0} \frac{G^E / RT}{x_1} = \lim_{x_1 \to 0} \frac{d(G^E / RT)}{dx_1}$$

From eqn(12.6)

$$\frac{d(G^E / RT)}{dx_1} = x_1 \frac{d \ln \gamma_1}{dx_1} + \ln \gamma_1 + x_2 \frac{d \ln \gamma_2}{dx_1} - \ln \gamma_2$$

■ Data Reduction

$\frac{G^E}{x_1 x_2 RT}$ => " linear "

Express this linear relation by the eqn.

$\frac{G^E}{x_1 x_2 RT} = A_{21}x_1 + A_{12}x_2$ (A_{21}, A_{12} => constant) $\Rightarrow \frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1 x_2$

since $\ln\gamma_1 = [\frac{\partial(nG^E/RT)}{\partial n_1}]_{P,T,n_2}$ (11.96)

We can derive expression for $\ln\gamma_1 \,\&\, \ln\gamma_2$

$\frac{nG^E}{RT} = (A_{21}n_1 + A_{12}n_2)\frac{n_1 n_2}{(n_1+n_2)^2}$, Differentiation wrt n_1

$$\ln\gamma_1 = n_2[(A_{21}n_1 + A_{12}n_2)(\frac{1}{(n_1+n_2)^2} - \frac{2n_1}{(n_1+n_2)^3}) + \frac{n_1 A_{21}}{(n_1+n_2)^2}]$$

Using $n_i = nx_i$

$$\ln\gamma_1 = x_2[(A_{21}x_1 + A_{12}x_2)(1-2x_1) + A_{21}x_1]$$, by inserting $x_2=1-x_1$

$$= x_2^2[A_{12} + 2(A_{21} - A_{12})x_1] \quad \text{(12-10a)}$$

similarly $$\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2] \quad \text{(12-10b)}$$

=> Margules equation

For the limiting conditions of infinite dilute solu (x_i -> 0)

$$\ln\gamma_1^\infty = A_{12} \ (x_1 = 0) \ , \ \ln\gamma_2^\infty = A_{21} \ (x_2 = 0)$$

Fig. 12.5 curve => $A_{12} = 0.372 , A_{21} = 0.198$

=> By linear regression of $\frac{G^E}{x_1x_2RT}$ data

$$\therefore \frac{G^E}{RT} = (0.198x_1 + 0.372x_2)x_1x_2$$

Margules eqn : can be used construction of correlation of original p-x_1-y_1 data set

From eqn (12.1) $y_1P = x_1\gamma_1P_1^{sat}$ and $y_2P = x_2\gamma_2P_2^{sat}$

$$\therefore P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat} \quad \text{(12-11)}$$

$$y_1 = \frac{x_1\gamma_1P_1^{sat}}{x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat}} \quad \text{(12-12)}$$

At given x_i -> obtain ┌ $_i$

Calculate p, y_i => Fig 12.5

Table 12.3 , Fig 12.6

=> Negative deviation from Raoult's Law

$$\gamma_i < 1 \quad \rightarrow \quad \ln \gamma_i < 0$$

Correlation by Morgules eqn -> not perfect

1) not suited to the data set in the limits as x_1 -> 0 x_1 ->1

2) P – x1 – y1 data : may not conform to the requirement of G/D eqn

■ Thermodynamic consistency

How well derived correlation is consistent with experimental data

– Experimental values of $\ln\gamma_1, \ln\gamma_2$ eqn (12.6) give the value of $\dfrac{nG^E}{RT}$

$$\frac{nG^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2 \qquad (12.6) \qquad \left(\gamma_i = \frac{y_i P}{x_i P_i^{sat}}\right) \qquad (12.1)$$

=> Independent of G/D eqn

If γ_i (Margules eqn) is derived from $\ln\gamma_1 = \left[\dfrac{\partial(nG^E/RT)}{\partial n_1}\right]_{P,T,n_j}$ (11.96)

=> Obey G/D eqn

∴ Derived γ_i may be inconsistent with experimental value unless experimental value satisfy G/D eqn

=> G/D is main criterion of thermodynamic consistency

- Test for the consistency

Write eqn (12.6) with experimental γ_i value obtained from eqn (12.1)

$$(\frac{G^E}{RT})^* = x_1 \ln\gamma_1^* + x_2 \ln\gamma_2^*$$

(* : experimental value)

By differential wrt x_1

$$\frac{d(G^E/RT)^*}{dx_1} = x_1\frac{d\ln\gamma_1^*}{dx_1} + \ln\gamma_1^* + x_2\frac{d\ln\gamma_2^*}{dx_1} - \ln\gamma_2^* = \ln\frac{\gamma_1^*}{\gamma_2^*} + x_1\frac{d\ln\gamma_1^*}{dx_1} + x_2\frac{d\ln\gamma_2^*}{dx_1}$$

In the case of derived eqn, it satisfy G/D eqn

$$\frac{d(G^E/RT)}{dx_1} = \ln\frac{\gamma_1}{\gamma_2} \qquad (x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0)$$

$$\frac{d(G^E/RT)}{dx_1} - \frac{d(G^E/RT)^*}{dx-1} = \ln\frac{\gamma_1^*}{\gamma_2^*} - \ln\frac{\gamma_1^*}{\gamma_2^*} - (x_1\frac{d\ln\gamma_1^*}{dx_1} + x_2\frac{d\ln\gamma_2^*}{dx_1})$$

Use δ notation to express difference

$$\frac{d\delta(G^E/RT)}{dx_1} = \delta\ln\frac{\gamma_1^*}{\gamma_2^*} - (x_1\frac{d\ln\gamma_1^*}{dx_1} + x_2\frac{d\ln\gamma_2^*}{dx_1})$$

If difference = 0 (which means correlation is consistent with exp data)

$$\delta \ln \frac{\gamma_1^*}{\gamma_2^*} = x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1} \qquad (12.13)$$

Measure of deviation from G/D eqn

If exp data satisfy G/D, right side = 0 = $\delta \ln \frac{\gamma_1^*}{\gamma_2^*}$

12.2. Models for the Excess Gibbs Energy

In general $\dfrac{G^E}{RT} = f(T, P, x_1, x_2 \ldots)$

For liquid, at low pressure, $\dfrac{G^E}{RT}$ is very weak function of P

$$\therefore \frac{G^E}{RT} = g(x_1, x_2 \ldots, x_N) \qquad \text{(at const. T)}$$

Margules' eqn. => one example of Models for G^E/RT

=> Only for mixture containing similar size shape and chemical nature coeff.

=> Can develop a number of equation for activity coeff.

For binary system

$$\frac{G^E}{x_1 x_2 RT} = a + bx_1 + cx_1^2 + \cdots \qquad \text{(at const. T)}$$

($x_2 = 1 - x_1$, x_1 is single independence variable)

Redlich/kister expansion

$$\frac{G^E}{x_1x_2RT} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots \quad (12.14) \quad \text{and} \quad \ln\gamma_i = [\frac{\partial(G^E/RT)}{\partial n_i}]_{P,T,n_j}$$

If A = B = C = ... = 0 , $\frac{G^E}{RT} = 0$, $\ln\gamma_1 = \ln\gamma_2 = 0$

$\gamma_1 = \gamma_2 = 1$ => Ideal solution

If B = C = ... = 0, $\frac{G^E}{x_1x_2RT} = A \Rightarrow \ln\gamma_1 = Ax_2^2 , \ln\gamma_2 = Ax_1^2$

If x_1-> 0 $\ln\gamma_1 \rightarrow \ln\gamma_1^\infty = A$

x_2-> 0 $\ln\gamma_2 \rightarrow \ln\gamma_2^\infty = A$

Margule's eqn

If C = ... = 0, $\frac{G^E}{x_1x_2RT} = A + B(x_1 - x_2) = A + B(2x_1 - 1)$

If A+B = A_{21}, A-B = A_{12} => Margule's eqn

$$\frac{G^E}{x_1x_2RT} = A_{21}x_1 + A_{12}x_2 \quad (12.9a)$$

=> two-const. Margule's eqn

van Laar Eqn.

Take reciprocal expression of $\frac{G^E}{x_1x_2RT} \Rightarrow \frac{x_1x_2RT}{G^E}$

and express $\frac{x_1x_2RT}{G^E}$ as a linear function of x_1

$$\frac{x_1x_2}{G^E/RT} = A'+B'(x_1 - x_2) = A'+B'(2x_1 - 1) \quad \text{or}$$

$$\frac{x_1x_2}{G^E/RT} = A'(x_1 + x_2) + B'(x_1 - x_2) = (A'+B')x_1 + (A'-B')x_2$$

define $B'+C' = 1/A'_{21}\ ,\ B'-C' = 1/A'_{12}$

$$\frac{x_1x_2}{G^E/RT} = \frac{x_1}{A'_{21}} + \frac{x_2}{A'_{12}} = \frac{A'_{12}\,x_1 + A'_{21}\,x_2}{A'_{12}\,A'_{21}}$$

$$\therefore \frac{G^E}{x_1x_2RT} = \frac{A'_{12}\,A'_{21}}{A'_{12}\,x_1 + A'_{21}\,x_2} \qquad (12\text{-}16)$$

For activity coeff. $\ln\gamma_1 = A'_{12}\,(1+\frac{A'_{21}\,x_1}{A'_{21}\,x_2})^{-2}\ ,\ \ln\gamma_2 = A'_{21}\,(1+\frac{A'_{21}\,x_2}{A'_{12}\,x_1})^{-2}$

When x_1 -> 0 , $\ln\gamma_1^{\infty} = A'_{12}$ -> find parameter

x_2 -> 0 , $\ln\gamma_2^{\infty} = A'_{21}$

In summary, the Redlich/Kister expansion, Margule's eqn. Van Larr eqn

=> Based on qn for G^E/x_1x_2RT using polynomials
=> Provide great flexibility in fitting VLE exp. Data for binary system
=> Limitation to apply multi-component system
=> Do not incorporate temperate dependency for the parameters

■ Local composition

Local – composition (introduced by Wilson)

- basis for molecular thermodynamics of liquid solution
- account for the short range order and non-random molecular orientation that result from differences in molecular size and intermolecular
- can correlate VLE data

Wilson Eqn – two parameter
NRTL (non-random – two – liquid) equation – 3 parameter
UNIQUAC (Universal Quasi – Chemical) equation – 2 parameter
UNIFAC –

■ Wilson eqn.

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + x_2\Lambda_{12}) - x_2 \ln(x_2 + x_1\Lambda_{21}) \qquad (12\text{-}18)$$

$$\ln\gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \qquad (12\text{-}19a)$$

$$\ln\gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \qquad (12\text{-}19b)$$

For infinite dilution $\ln\gamma_1^\infty = -\ln\Lambda_{12} + 1 - \Lambda_{21}$, $\ln\gamma_2^\infty = -\ln\Lambda_{21} + 1 - \Lambda_{12}$

■ NRTL eqn.

$$\frac{G^E}{x_1 x_2 RT} = \frac{G_{21}\tau_{12}}{x_1 + x_2 G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1 G_{12}} \qquad (12\text{-}20)$$

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{(x_2 + x_1 G_{12})^2}\right] \qquad (12\text{-}21a)$$

$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{(x_1 + x_2 G_{21})^2}\right] \qquad (12\text{-}21b)$$

where $G_{12} = \exp(-\alpha\tau_{12})$, $G_{21} = \exp(-\alpha\tau_{21})$, $\tau_{12} = \frac{b_{12}}{RT}$, $\tau_{21} = \frac{b_{21}}{RT}$

(α , b_{12} , b_{21} -> parameters specific to a particular pair of species

$$\ln\gamma_1^{\infty} = \tau_{21} + \tau_{12}\exp(-\alpha\tau_{12}) \qquad \ln\gamma_2^{\infty} = \tau_{12} + \tau_{21}\exp(-\alpha\tau_{21})$$

※ UNIQUAC, UNIFAC => See Appendix H

12-3 Property Changes of Mixing

From (11.79) to (11.82) => expression for the ideal solution

$$G^{id} = \sum x_i G_i - RT \sum x_i \ln x_i \quad (11.79) \qquad V^{id} = \sum x_i V_i \quad (11.81)$$

$$S^{id} = \sum x_i S_i - R \sum x_i \ln x_i \quad (11.80) \qquad H^{id} = \sum x_i H_i \quad (11.82)$$

By using definition of excess property $M^E = M - M^{id}$

$$G^E = G - \sum_i x_i G_i - RT \sum_i x_i \ln x_i$$

$$S^E = S - \sum_i x_i S_i - R \sum_i x_i \ln x_i$$

$$V^E = V - \sum_i x_i V_i \qquad \rightarrow M - \sum x_i M_i$$ => Property change of mixing

$$\Delta M = M - \sum_i x_i M_i$$

$$H^E = H - \sum_i x_i H_i$$

$$\therefore G^E = \Delta G - RT \sum_i x_i \ln x_i \qquad S^E = \Delta S - R \sum_i x_i \ln x_i$$

$$V^E = \Delta V \qquad H^E = \Delta H$$

For ideal solution , $M^E = 0$

$$\therefore \Delta G^{id} = RT \sum_i x_i \ln x_i \qquad \Delta S^{id} = R \sum_i x_i \ln x_i$$

$$\Delta V^{id} = 0 \qquad \Delta H^{id} = 0$$

since $\Delta M^{id} = M^{id} - \sum_i x_i M_i$

$$\Delta M - \Delta M^{id} = M - M^{id} = M^E$$

Focusing on △V, △H

1) Can measure directly from the experiment
2) Identical with excess property

○ Mixing ->
- Movement of piston -> change of volume
  (to maintain cause P)
- Add or extract heat -> change of entropy
  (to maintain cause T)

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○ After mixing is completed

- Total volume change $\Delta V^t = (n_1 + n_2)V - n_1V_1 - n_2V_2$
- Total entropy change $\Delta H^t = Q$ at const P.

$$d(nU) = dQ + dW, \qquad dQ = d(nU) + Pd(nV)$$

$$(dW = -Pd(nV)) \qquad = d(n(U + PV)) = dH$$

$$\therefore Q = \Delta H^t = (n_1 + n_2)H - (n_1H_1 - n_2H_2)$$

$$\therefore \Delta V \equiv \frac{\Delta V^t}{n_1 + n_2} = V - x_1V_1 - x_2V_2$$

$$\Delta H \equiv \frac{Q}{n_1 + n_2} = H - x_1H_1 - x_2H_2$$ => Heat of mixing

∴ can calculate $\triangle V$, $\triangle H$ from experiment ($\triangle V^t$, Q)

H^E or V^E can be express by eqn similar to those used for G^E data
(Redlich / Kister expansion

12.4 Heat effects of mixing processes

○ The heat of mixing : $\Delta H = H - \sum_i x_i H_i$

$$H = x_1 H_1 + x_2 H_2 + \Delta H$$

(Calculate entropy of solution from entropy of pure species and heat of mixing)

“ Heat of mixing vs. Heat of reaction.”

○ Heats of solution

- Heat effect by dissolving solid or gas in liquid
- Based on the dissolution of 1 mol of solute
  if species 1 is the solute, x_1 : the moles of solute/mole of solution

△H : heat effect/mol of solution $\Delta H = \dfrac{I}{n_1 + n_2}$

△H/x_1 : heat effect/mol of solute $\Delta \tilde{H} = \dfrac{J}{n_1 + n_2} \times \dfrac{n_1 + n_2}{n_1} = \Delta H \times \dfrac{1}{x_1}$

■ Example of solution processes

$$\mathrm{LiCl(s)} + 12\mathrm{H_2O(l)} \rightarrow \underline{\mathrm{LiCl(12H_2O)}} \qquad , \Delta\tilde{H} = -33614\mathrm{J}$$

Solution of 1 mol of LiCl dissolved in 12 mole of H_2O

$\Delta\tilde{H} = -33614\mathrm{J}$ => Enthalpy of 1 mol of LiCl in 12 mol of H2O is 33614J less than combined enthalpy of 1 mol of pure LiCl (s) and 12 mol of pure H_2O (l)

- Heat of solution is calculated from the heats of formation

Enthalpy/Concentration (Hx) Diagrams

Hx diagram : plot enthalpy vs composition
temperature is parameter, constant pressure

Enthalpy -> based on a unit mass of solution

$$H = x_1 H_1 + x_2 H_2 + \Delta H$$

∴ H is dependent on $\Delta H + (H_1, H_2)$

- absolute enthalpies are unknown (=> need zero point for pure species)
  => the basis of an Hx diagram is $H_1 = 0$, $H_2 = 0$

In Figure 12. 17

$H_1 = 0$ for pure water at the triple point ($\approx 32^{o}5$)
$H_2 = 0$ for pure H_2SO_4 at $25^{o}C$

※ The advantage of taking H = 0 for pure liq water at its triple point is that this is the base of steam table.

H/x diagram vs adiabetic mixing of solution

=> H/x diagram : when all solution is formed by adiabetic mixing

assumption : 1. no shaft work, no E_K, no E_P

2. a, b -> two initial binary solution

c -> Final solution

$$\Delta H^t = Q = 0 \quad (\Delta H + E_K + E_P) = Q + W_S \ (2.32a)$$

Energy balance $\therefore (n^a + n^b)H^c = n^a H^a + n^b H^b$

Material Balance for species 1 $(n^a + n^b)x_1^c = n^a x_1^a + n^b x_1^b$

By rearrangement

$$n^a(H^c - H^a) = -n^b(H^c - H^b) \quad ① \qquad n^a(x_1^c - x_1^a) = -n^b(x_1^c - x_1^b) \quad ②$$

Division of eqn ① by ② $\dfrac{H^c - H^a}{x_1^c - x_1^a} = \dfrac{H^c - H^b}{x_1^c - x_1^b}$

※ Show that the three point (c , a , b) $(H^c, x_1^c), (H^a, x_1^a), (H^b, x_1^b)$ lie along a straight line on an Hx diagram.

Assume that eqn for straight line.

$$H = mx_1 + k \quad \text{(B)}$$

If line passes through point a and b

$$H^a = mx_1^a + k\,,\; H^b = mx_1^b + k$$

Subtract two equation from eqn (B)

$$H - H^a = m(x_1 - x_1^a)\,,\; H - H^b = m(x_1 - x_1^b)$$

By division

$$\frac{H - H^a}{H - H^b} = \frac{x_1 - x_1^a}{x_1 - x_1^b} \quad \rightarrow \quad \frac{H - H^a}{x_1 - x_1^a} = \frac{H - H^b}{x_1 - x_1^b}$$