Chemical Engineering Thermodynamics

Solution Thermodynamics:

Models for γ_i *and* The Gamma/Phi Formulation

Property Change of Mixing

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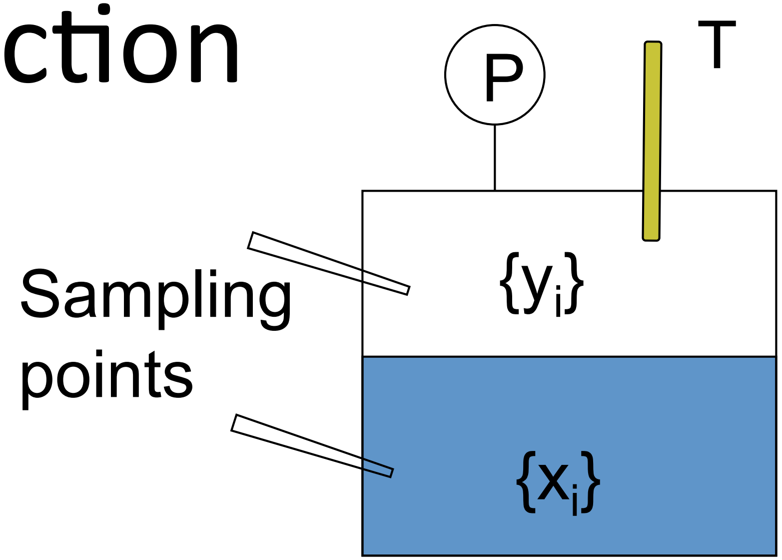
This Chapter Learning Outcomes

1. Knows how to collect VLE data from experiment
2. Able to calculate γ_i from the VLE data
3. Able to develop correllation for γ_i from the VLE data
4. Knows how to use the VLE data to determine correlation's parameters
5. Familiar with the commonly available correlations for γ_i

VLE Data Collection



VLE criteria,

$$\hat{f}_i^l = \hat{f}_i^v$$

$$\gamma_i x_i f_i = \hat{\phi}_i y_i P$$

If gas phase is an ideal-gas mixture,

we get modified Raoult's Law (see chapter 10),

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

note: at azeotrope $y_i = x_i$, so $\gamma_i^{az} = \dfrac{P^{az}}{P_i^{\text{sat}}}$

Method to Predict γ_i

Let's go to the lab and carry out an experiment to get VLE data (P, x_1, y_1) for Chloroform(1) / 1,4-Dioxane(2) at T=50^{o}C

Note:

The pressure is low,
so we could assume an ideal-gas mixture, hence could use the Modified Raoult's Law

Plot of Px_1y_1 diagram is on Figure 12.6(a)

We will now develop a correlation of γ_i from the data.

We are going to see specifically how the Margules Eqn was developed.

This is a data reduction method (Empirical).

First we will use the VLE data for the binary system to,

1. Calculate γ_1 and γ_2 from Modified Raoult's Law
2. Calculate $\ln\gamma_1$ and $\ln\gamma_2$
3. Calculate $\frac{G^E}{RT}$ and $\frac{G^E}{x_1 x_2 RT}$:

Eqn 11.99 for binary system,

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

Divide both side by $x_1 x_2$

$$\frac{G^E}{x_1 x_2 RT} = \frac{1}{x_1 x_2}(x_1 \ln\gamma_1 + x_2 \ln\gamma_2)$$

From the VLE data, we tabulate

$$\ln\gamma_1 \qquad \ln\gamma_2 \qquad \frac{G^E}{RT} \qquad \frac{G^E}{x_1 x_2 RT}$$

Plot $\ln\gamma_1$ vs x_1

Plot $\ln\gamma_2$ vs x_1

Plot G^E/RT vs x_1

Plot G^E/x_1x_2RT vs x_1

These are represented by the dotted points in Fig 12.6(b).

Also plot P vs x_1 and P vs y_1 i.e. Px_1y_1 diagram.

These are represented by the dotted points in Fig 12.6(a).

Note in Fig 12.6(b): Plot G^E/x_1x_2RT vs x_1 is more linear than others.

Let's gives the following mathematical linear relation,

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

when $x_1 = 1,\ x_2 = 0$ $\quad \frac{G^E}{x_1x_2RT} = -1.27 = A_{21}(1) + A_{12}(0)$

when $x_1 = 0,\ x_2 = 1$ $\quad \frac{G^E}{x_1x_2RT} = -0.72 = A_{21}(0) + A_{12}(1)$

so

$A_{21} = -1.27 \qquad A_{21} = -0.72$

i.e. intersections on vertical axis at both ends.

Rearrange 12.9a,

$$\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2 \qquad (12.9b)$$

then multiply n on left side and nn^2 / n^2 on the rightside

$$\frac{nG^E}{RT} = n(A_{21}x_1 + A_{12}x_2)\,\frac{\mathrm{n}x_1 n x_2}{n^2}$$

$$=(A_{21}n_1 + A_{12}n_2)\frac{n_1 n_2}{n^2}$$

Substitute into eqn 11.96,

$$\ln\gamma_1 = \left[\frac{\partial\left(\dfrac{nG^E}{RT}\right)}{\partial n_1}\right]_{P,T,n_2} = \left[\frac{\partial\left((A_{21}n_1 + A_{12}n_2)\dfrac{n_1 n_2}{n^2}\right)}{\partial n_1}\right]_{P,T,n_2}$$

$$= \left(A_{21}n_1 + A_{12}n_2\right)\left(\frac{n_2}{n^2} + n_1 n_2(-2n^{-3})\right) + \frac{n_1 n_2 A_{21}}{n^2}$$

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

$$\ln\gamma_1 = n_2\left[\left(A_{21}n_1 + A_{12}n_2\right)\left(\frac{1}{n^2} - \frac{2n_1}{n^3}\right) + \frac{n_1A_{21}}{n^2}\right]$$

for $n_i = x_in$

$$\ln\gamma_1 = x_2\left[\left(A_{21}x_1 + A_{12}x_2\right)\left(1 - 2x_1\right) + x_1A_{21}\right]$$

$$= x_2\left[A_{21}x_1 - 2A_{21}x_1^2 + A_{12}x_2 - 2A_{12}x_1x_2 + x_1A_{21}\right]$$

$$= x_2\left[2A_{21}x_1 - 2A_{21}x_1^2 - 2A_{12}x_1x_2 + A_{12}x_2\right]$$

$$= x_2\left[2A_{21}x_1(1 - x_1) - 2A_{12}x_1x_2 + A_{12}x_2\right]$$

$$= x_2\left[2A_{21}x_1x_2 - 2A_{12}x_1x_2 + A_{12}x_2\right]$$

$$= x_2^2\left[2(A_{21} - A_{12})x_1 + A_{12}\right] \qquad (12.10a)$$

So we get the correlation for activity coefficient,

$$\ln\gamma_1 = x_2^2\left[A_{12} + 2(A_{21} - A_{12})x_1\right] \qquad (12.10a)$$

Similarly, differentiate Eqn 12.9b with respect to component 2 will give,

$$\ln\gamma_2 = x_1^2\left[A_{21} + 2(A_{12} - A_{21})x_2\right] \qquad (12.10b)$$

Note: All these were derived from,

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

Eqn 12.9a,12.10a, 12.10b are the Margules Equations !!!!

For various values of x_1 and the experimental data for vapor pressures (P^{sat}), and using A_{12}=-0.72 and A_{21}=-1.27,

1. Recalculate y_1 and P using BUBL P calculation and Modified Raoult's Law.

2. Recalculate $\ln\gamma_1$, $\ln\gamma_2$, G^E/RT , G^E/x_1x_2RT using the Margules correlations.

and replot the VLE diagrams for Chloroform(1)/1,4-Dioxane(2) at T=50^{o}C.

These are represented by solid lines in Fig 12.6. Observe that the correlations fit the data very well.

Other Empirical Models for γ_i

The Redlich/Kister Expansion

$$\frac{G^E}{x_1 x_2 RT} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots\ldots \qquad (12.14)$$

For truncation after one term,

$$\frac{G^E}{x_1 x_2 RT} = A$$

Apply eqn 11.96 to give,

$$\ln \gamma_1 = A x_2^2 \qquad \ln \gamma_2 = A x_1^2 \qquad (12.15a,b)$$

Note: This is the correlation used in example 10.3

Where at infinite dilution,

$$\ln \gamma_1^\infty = \ln \gamma_2^\infty = A$$

For truncation after two terms,

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

If we define A_{21} = A+B , A_{12} = A-B ....(a)

we can show that this is equal to Margules Eqn.

Substitute (a) into Margules Eqn, we get

$$\frac{G^E}{x_1 x_2 RT} = (A + B)x_1 + (A - B)x_2 = Ax_1 + Bx_1 + Ax_2 - Bx_2$$

$$= A(x_1 + x_2) + B(x_1 - x_2) = A + B(x_1 - x_2)$$

van Laar Equations

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

let

$$A' + B' = \frac{1}{A'_{21}} \quad \text{and} \quad A' - B' = \frac{1}{A'_{12}}$$

so,

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

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

Apply Eqn 11.96, we get

$$\ln\gamma_1 = A'_{12}\left(1 - \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2} \qquad (12.17a)$$

$$\ln\gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2} \qquad (12.17b)$$

At infinite dilution,

when $x_1 = 0 \quad \ln\gamma_1^{\infty} = A'_{12}$

when $x_2 = 0 \quad \ln\gamma_2^{\infty} = A'_{21}$

Features of Margules, Redlich/Kister and van Laar Equations

Applicable to binary mixture only

Empirical (fitting VLE data)

No theoretical foundation

Υ_i is independent of pressure

Applicable at constant T

Other γ_i models:

Local Composition Models

Local Composition Models

The first of these models was introduced in 1964 by G.M. Wilson and known as the Wilson equation.

Next comes the NRTL (Non-Random-Two-Liquid) by Renon and Prausnitz.

After that is the UNIQUAC (Universal Quasi-Chemical) by Abrams and Prausnitz.

Later on, the UNIFAC (an improved version of UNIQUAC) that is based on molecular groups' contribution.

The Wilson equation

$$\frac{G^E}{RT} = -\sum_i x_i \left(\ln \sum_j x_j \Lambda_{ij} \right) \qquad (12.22)$$

from this we will get the correlation for gamma,

$$\ln \gamma_i = 1 - \ln \left(\sum_j x_j \Lambda_{ij} \right) - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \qquad (12.23)$$

where

$$\Lambda_{ij} = 1 \qquad \text{for} \quad i = j$$

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp \frac{-a_{ij}}{RT} \qquad (i \neq j) \qquad (12.24)$$

a_{ij} is binary parameters and

V_i is molar volume of pure liquid i at T

Apply Wilson equation to a binary system,

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

that gives,

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

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

where

$$\ln\gamma_1^\infty = -\ln\Lambda_{12} + 1 - \Lambda_{21} \qquad \ln\gamma_2^\infty = -\ln\Lambda_{21} + 1 - \Lambda_{12}$$

See equations 12.20, 12.21a, 12.21b etc for NRTL equation.

More information on UNIQUAC and UNIFAC in Appendix H.

The Gamma/Phi Formulation

VLE Criteria for Multicomponent System

$$\hat{f}_i^l = \hat{f}_i^v$$

So,

$$\gamma_i x_i f_i = \hat{\phi}_i y_i P$$

We know that,

$$f_i = f_i^l = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l (P - P_i^{sat})}{RT} \qquad (11.44)$$

Substitute,

$$\gamma_i x_i \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l (P - P_i^{sat})}{\mathrm{RT}} = \hat{\phi}_\mathrm{i} y_i P$$

Rearrange,

$$\gamma_i x_i P_i^{sat} = \frac{\hat{\phi}_\mathrm{i} y_i P}{\phi_i^{sat} \exp \frac{V_i^l (P - P_i^{sat})}{\mathrm{RT}}}$$

$$= \left[\frac{\hat{\phi}_\mathrm{i}}{\phi_i^{sat}} \exp \frac{-V_i^l (P - P_i^{sat})}{\mathrm{RT}} \right] y_i P$$

Define,

$$\Phi_i = \left[\frac{\hat{\phi}_i}{\phi_i^{sat}} \exp \frac{-V_i^l (P - P_i^{sat})}{RT} \right] \qquad (14.0)$$

Then, we get
the Gamma/Phi formulation,

$$\gamma_i x_i P_i^{sat} = \Phi_i y_i P \qquad (14.1)$$

At low to moderate pressure,

$$\exp \frac{-V_i^l (P - P_i^{sat})}{RT} \approx 1$$

So,

$$\Phi_i = \frac{\hat{\phi}_i}{\phi_i^{sat}} \qquad (14.2)$$

For low to moderate pressure, we can use two-term Virial EOS,

$$\hat{\phi}_i = \exp\left[\frac{P}{RT}\left(B_{ii} + \tfrac{1}{2}\sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk})\right)\right] \qquad (11.64 \ \& \ 14.4)$$

where

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad \text{and} \quad \delta_{jk} = 2B_{jk} - B_{jj} - B_{kk}$$

$$\delta_{ii} = \delta_{jj} = 0 \quad \text{and} \quad \delta_{ij} = \delta_{ji}$$

$$B_{ij} = \frac{RT_{cij}}{P_{cij}}\left(B^0 + \omega_{ij} B^1\right) \qquad \omega_{ij} = \frac{\omega_i + \omega_j}{2} \qquad T_{cij} = (T_{ci} T_{cj})^{1/2}(1 - k_{ij})$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}} \qquad Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \qquad V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3$$

Also,

$$\phi_i^{sat} = \phi_i = exp\left[\frac{B_{ii}P_i^{sat}}{RT}\right] \qquad (11.36 \ \& \ 14.5)$$

$$Note: B_{ii} = B$$

Where, eqn 3.62 and 3.63 give,

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1 \qquad (3.63)$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \text{and} \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Therefore eqn (14.0) becomes,

$$\Phi_i = \frac{\hat{\phi}_i}{\phi_i^{sat}} = \frac{\exp\left[\frac{P}{RT}\left(B_{ii} + \frac{1}{2}\sum_j\sum_k y_j y_k (2\delta_{ji} - \delta_{jk})\right)\right]}{exp\left[\frac{B_{ii}P_i^{sat}}{RT}\right]}$$

$$= \exp\left[\frac{P}{RT}\left(B_{ii} + \frac{1}{2}\sum_j\sum_k y_j y_k (2\delta_{ji} - \delta_{jk})\right) - \frac{B_{ii}P_i^{sat}}{RT}\right]$$

$$= \exp\left[\frac{B_{ii}(P - P_i^{sat}) + \frac{1}{2}P\sum_j\sum_k y_j y_k (2\delta_{ji} - \delta_{jk})}{RT}\right] \qquad (14.6)$$

Apply to binary system,

$$\Phi_1 = \exp\left[\frac{B_{11}(P - P_1^{sat}) + P y_2^2 \delta_{12}}{RT}\right] \qquad (14.7a)$$

$$\Phi_2 = \exp\left[\frac{B_{22}(P - P_2^{sat}) + P y_1^2 \delta_{12}}{RT}\right] \qquad (14.7b)$$

Note: We could use the following eqn that is based on generic cubic EOS to fugacity coefficient for species i in solution or mixture,

$$\ln \hat{\phi}_i = \frac{b_i}{b}(Z-1) - \ln(Z-\beta) - \bar{q}_i I \qquad (14.50)$$

the Gamma/Phi formulation,

$$\gamma_i x_i P_i^{sat} = y_i \Phi_i P$$

For ideal gas mixture, in equilibrium with non-ideal liquid solution $\Phi_i = 1$

$$\gamma_i x_i P_i^{sat} = y_i P \qquad \text{Modified Raoult's Law}$$

For ideal gas mixture in equilibrium with ideal liquid solution $\gamma_i = \Phi_i = 1$

$$x_i P_i^{sat} = y_i P \qquad \text{Raoult's Law}$$

$$\gamma_i x_i P_i^{sat} = y_i \Phi_i P$$

For VLE calculation, we need

$\Phi_i = \Phi(T, P, y_1, y_2, \ldots. y_{N-1})$ such eqn 14.6

$\gamma_i = \gamma(T, x_1, x_2, \ldots. x_{N-1})$ see chap 12 for correlations

$P_i^{sat} = f(T)$ such as Antoine Eqn

Bubblepoint Calculations

$$\sum_{i} x_i K_i = \sum x_i \frac{\gamma_i P_i^{sat}}{\Phi_i P} = 1 \qquad y_i = \frac{\gamma_i x_i P_i^{sat}}{\Phi_i P} \qquad (14.8)$$

Bubble pressure calculation,

$$P = \sum_{i} x_i \frac{\gamma_i P_i^{sat}}{\Phi_i} \qquad (14.10)$$

Bubble temperature calculation,

$$P_j^{sat} = \frac{P}{\sum_{i} \frac{x_i \gamma_i}{\Phi_i} \frac{P_i^{sat}}{P_j^{sat}}} \qquad (14.13)$$

Since $\{y_i\}$ is not known, we can't evaluate Φ_i . Calculation needs iteration (single loop). For algorithm, see the following Figure 14.1 and 14.3

Dewpoint Calculation

$$\sum_i \frac{y_i}{K_i} = \sum \frac{y_i}{\dfrac{\gamma_i P_i^{sat}}{\Phi_i P}} = 1$$

$$x_i = \frac{y_i \Phi_i P}{\gamma_i P_i^{sat}} \qquad (14.9)$$

Dew pressure calculation,

$$P = \frac{1}{\sum \dfrac{y_i \Phi_i}{\gamma_i P_i^{sat}}} \qquad (14.11)$$

Since $\{x_i\}$ and P are not known, we can't evaluate Υ_i and ϕ_i . Calculation needs iteration (double loop).
For algorithm, see Figure 14.2

Dew temperature calculation,

$$P_j^{sat} = P \sum \frac{y_i \Phi_i}{\gamma_i} \frac{P_j^{sat}}{P_i^{sat}} \qquad (14.14)$$

Since $\{x_i\}$ and T are not known, we can't evaluate Υ_i and ϕ_i . Calculation needs iteration (double loop).
For algorithm, see Figure 14.4

Flash Calculations

$$y_i = \frac{z_i K_i}{1+V(K_i-1)} \qquad (10.16)$$

$$F_y = \sum y_i - 1 = \sum \frac{z_i K_i}{1+V(K_i-1)} - 1 = 0 \qquad (10.17) \text{ or } (14.17)$$

$$x_i = \frac{z_i}{1+V(K_i-1)} \qquad (14.16)$$

$$F_x = \sum x_i - 1 = \sum \frac{z_i}{1+V(K_i-1)} - 1 = 0 \qquad (10.17) \text{ or } (14.17)$$

$$F = F_x - F_y = 0$$

$$F = \sum \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0 \qquad (14.19)$$

$$\frac{dF}{dV} = -\sum \frac{z_i(K_i - 1)^2}{\left[1 + V(K_i - 1)\right]^2} \qquad (14.20)$$

So, dF/dV is always negative, hence the F vs. V is monotonic.

This will give rapid convergence for iteration with Newton's method.

$$F + \left(\frac{dF}{dV}\right)\Delta V = F + \left(\frac{dF}{dV}\right)(V_{n+1} - V_n) = 0 \qquad (14.21)$$

Solution Thermodynamics:

Property Change of Mixing

Property Changes of Mixing

From definition of excess property (Chap 11):

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

$$G^E = G - G^{id} = G - \left(\sum x_i G_i + RT \sum x_i \ln x_i\right)$$
$$= \Delta G_{mix} - RT \sum x_i \ln x_i$$

$$S^E = S - S^{id} = S - \left(\sum x_i S_i - R \sum x_i \ln x_i\right)$$
$$= \Delta S_{mix} + R \sum x_i \ln x_i$$

$$V^E = V - V^{id} = V - \sum x_i V_i = \Delta V_{mix}$$

$$H^E = H - H^{id} = H - \sum x_i H_i = \Delta H_{mix}$$

Property Changes of Mixing

$$\Delta M_{mix} = M - \sum x_i M_i$$

For ideal solution $M^E = 0$, so

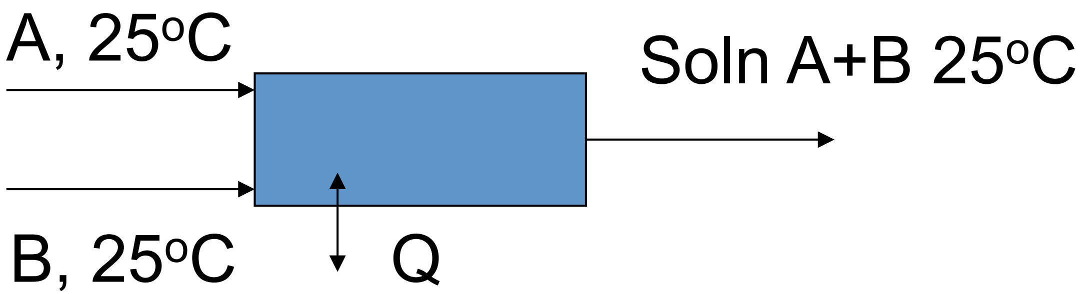
$$\Delta G_{mix} = RT \sum x_i \ln x_i$$

$$\Delta S_{mix} = -R \sum x_i \ln x_i$$

$$\Delta H_{mix} = 0$$

$$\Delta V_{mix} = 0$$

Example: Ideal Solution



Energy Balance:

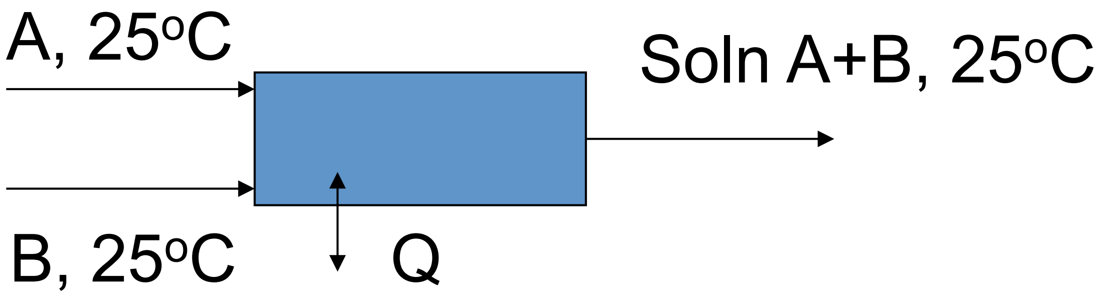
$$\dot{Q} - \dot{W} = \Delta\dot{H} + \Delta\dot{E}_{KE} + \Delta\dot{E}_{PE} = \Delta\dot{H}$$

$$\dot{Q} = \dot{H}_{out} - \dot{H}_{in} = \dot{m}_{A+B}H^{id} - \dot{m}_A H_A - \dot{m}_B H_B$$

$$\dot{Q} = \dot{H}^{id} - \sum \dot{m}_i H_i = \sum \dot{m}_i H_i - \sum \dot{m}_i H_i$$

$$\dot{Q} = 0$$

Example: Non-Ideal Solution



Energy Balance

$$\dot{Q} - \cancel{\dot{W}} = \Delta\dot{H} + \cancel{\Delta\dot{E}_{KE}} + \cancel{\Delta\dot{E}_{PE}} = \Delta\dot{H}$$

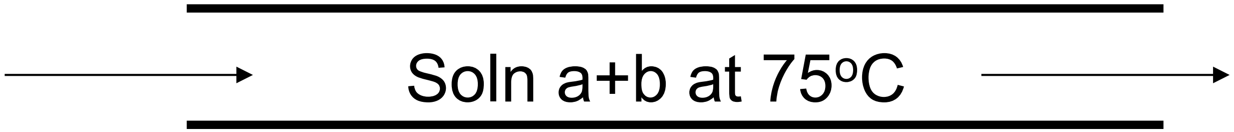
$$\dot{Q} = \dot{m}_{A+B}H - \dot{m}_A H_A - \dot{m}_B H_B = \dot{m}_{A+B}H - \sum \dot{m}_i H_i$$

$$\dot{Q} = (\Delta\dot{H}_{mix} + \cancel{\sum \dot{m}_i H_i}) - \cancel{\sum \dot{m}_i H_i}$$

$$\dot{Q} = \Delta\dot{H}_{mix}$$

If the system is adiabatic, what will be the outlet temperature?

Example Non-Ideal Solution



A non-ideal solution of a+b flow in a pipe.

Determine the stream enthalpy (H)

$$\mathrm{H} = \Delta \mathrm{H}^{0}_{\mathrm{f},298} + C_P \Delta T$$

We need,

1) Heat of formation of the solution!!!!

2) Heat capacity of the solution.

Heat Effects of Mixing Processes

Two ways to solve energy balance involving the heat of mixing,

1. Use the enthalpy of solution (H)

2. Use the heat of mixing (ΔH_{mix})

1. Enthalpy of Solution (*H*)

From eqn 12.39,

$$H = \Delta H_{mix} + \sum x_i H_i$$

H could be found by using Hx diagram such as Figure 12.17 (H_2SO_4/H_2O), Figure 12.19 ($NaOH/H_2O$).

Example 12.6

Unit Operation: Evaporator

SSSF Mass Balance: In = Out

Overall Mass Balance: $\dot{m}_1 = \dot{m}_2 + \dot{m}_3$

Component i Mass Balance: $x_{i,1}\dot{m}_1 = x_{i,2}\dot{m}_2 + x_{i,3}\dot{m}_3$

Component Mass Balance,

For NaOH: $0.1(10,000) = 0.5\dot{m}_2 + 0(\dot{m}_3)$ $\dot{m}_2 = 2000\,\frac{lb_m}{hr}$

For H_2O: $0.9(10,000) = 0.5(2,000) + 1(\dot{m}_3)$ $\dot{m}_3 = 8,000\,\frac{lb_m}{hr}$

Energy Balance,

$$\dot{Q} = \Delta\dot{H} = \dot{H}_{out} - \dot{H}_{in} = \dot{m}_3 H_3 + \dot{m}_2 H_2 - \dot{m}_1 H_1$$

From Hx diagram (Fig 12.19) and steam table,

$$\dot{Q} = 8000(1146) + 2000(215) - 10000\,\frac{lb_m}{hr}(34\,\frac{BTU}{lb_m})$$

$$\dot{Q} = 926000\,\frac{BTU}{hr}$$ Heat duty of the evaporator

Note: Reference conditions for H_2O for the NaOH Hx diagram (Fig 12.19) is similar to the textbook's Steam Table

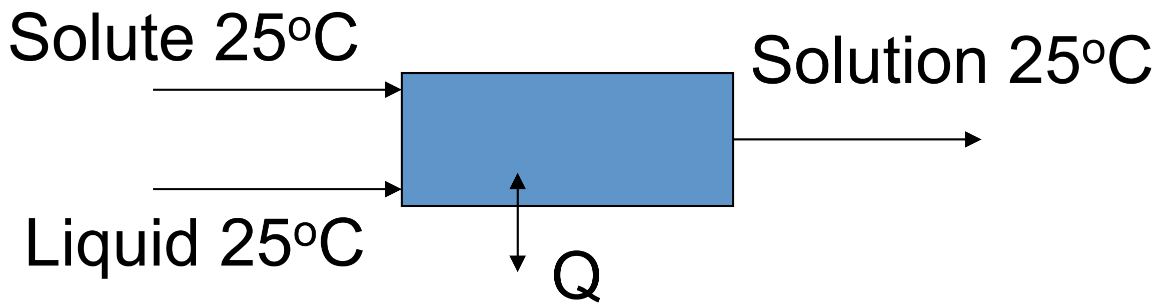
If we do not have Hx diagram, use

2. Calculate ΔH_{mix} using heat of solution or heat of formation of solution

$$\Delta \tilde{H}_{298}$$

$$\Delta H^{o}_{f,298}$$

*H*eat of solution ($\Delta\tilde{H}_{298}$) diagram, Figure 12.14



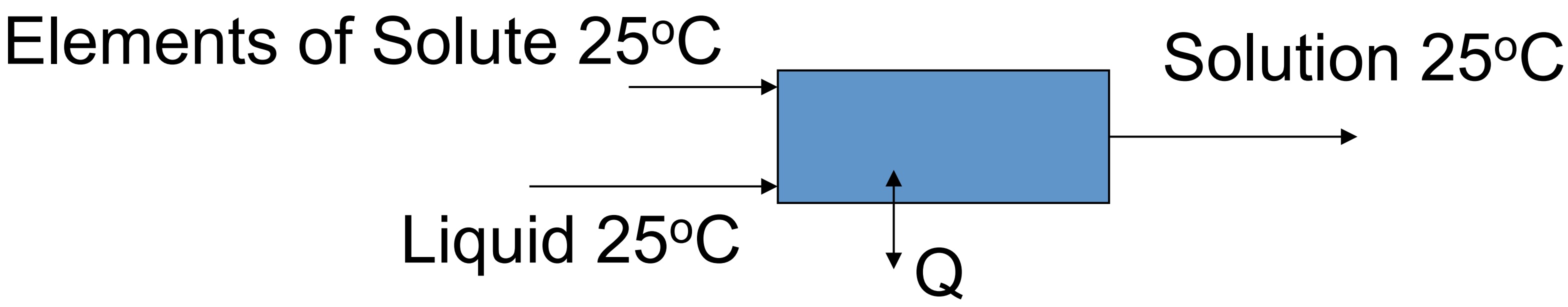
As shown before, $Q = \Delta H_{mix} = H - \sum x_i H_i$

Example: $\mathrm{LiCl(s) + 12H_2O(l) \rightarrow LiCl(12H_2O)}$

$\Delta\tilde{H}_{298} = -33{,}614 J$ (basis per mol solute), see Fig 12.14

$\Delta H_{mix,298} = n_{solute}\Delta\tilde{H}_{298}$

Heat of formation of solution ($\Delta H^o_{f,298}$),



Example: $Li + \frac{1}{2}Cl_2 + 12H_2O(l) \rightarrow LiCl(12H_2O)$

See page 457

$\Delta H^0_{f,298} = -442{,}224\,J$ (Basis per 1 mol of LiCl in 12 mols H_2O)

Note: Referent condition for H_2O is liquid at 25°C

(not its elements)

To calculate heat of solution ($\Delta\tilde{H}_{298}$)

from heat of formation of solution ($\Delta H^0_{f,298}$),

$$\mathrm{Li} + \tfrac{1}{2}\mathrm{Cl_2} + 12\mathrm{H_2O(l)} \rightarrow \mathrm{LiCl(12H_2O)} \quad \Delta H^0_{f,298} = -442{,}224\,J$$

$$+ \quad \mathrm{LiCl(s)} \rightarrow \mathrm{Li} + \tfrac{1}{2}\mathrm{Cl_2} \quad -\Delta H^0_{f,298} = 408{,}610\,J$$

– –

$$\mathrm{LiCl(s)} + 12\mathrm{H_2O(l)} \rightarrow \mathrm{LiCl(12H_2O)} \quad \Delta\tilde{H}_{298} = -33{,}614\,J$$

To calculate heat of formation of solution $(\Delta H^{0}_{f,298})$

from heat of solution $(\Delta \tilde{H}_{298})$,

$$\mathrm{Li} + \tfrac{1}{2}\mathrm{Cl_2} \rightarrow \mathrm{LiCl(s)} \qquad \Delta H^{0}_{f,298} = -408{,}610J$$

$$+ \quad \mathrm{LiCl(s)} + 12\mathrm{H_2O(l)} \rightarrow \mathrm{LiCl(12H_2O)} \qquad \Delta \tilde{H}_{298} = -33{,}614J$$

– –

$$\mathrm{Li} + \tfrac{1}{2}\mathrm{Cl_2} + 12\mathrm{H_2O(l)} \rightarrow \mathrm{LiCl(12H_2O)} \qquad \Delta H^{0}_{f,298} = -442{,}224J$$

Example 12.5

This example uses Figure 12.14 for ΔH_{mix},

SSSF Mass Balance: In = Out

Overall Mass Balance: $\dot{m}_1 = \dot{m}_2 + \dot{m}_3$

Component *i* Mass Balance: $x_{i,1}\dot{m}_1 = x_{i,2}\dot{m}_2 + x_{i,3}\dot{m}_3$

Component Mass Balance,

For LiCl: $0.15(2) = 0.4\dot{m}_2 + 0(\dot{m}_3)$ $\dot{m}_2 = 0.75 kg/s$

For H_2O: $0.85(2) = 0.6(0.75) + 1(\dot{m}_3)$ $\dot{m}_3 = 1.25 kg/s$

SSSF Energy Balance,

$$\dot{Q} = \Delta\dot{H} = \dot{m}_3 H_3 + \dot{m}_2 H_2 - \dot{m}_1 H_1$$

where:

$H_2 = \Delta H_{mix} + \sum x_i H_i$ at 132°C

$H_1 = \Delta H_{mix} + \sum x_i H_i$ at 25°C

We do not have enthalpy of solution data

H_3 Enthalpy water vapor at 132°C

Since we only have heat of solution data at 25°C (Fig 12.14), we need to apply hyphothetical or calculational path.

Energy Balance,

$$\dot{Q} = \dot{m}_3 H_3 + \dot{m}_2 H_2 - \dot{m}_1 H_1$$

$$= \Delta\dot{H}^t$$

$$= \Delta\dot{H}^t_a + \Delta\dot{H}^t_b + \Delta\dot{H}^t_c + \Delta\dot{H}^t_d$$

UTM

$\Delta\dot{H}_a^t$: Unmixing process

Mole entering,

$$\frac{0.03\text{kg}(1000\text{g/kg})}{42.39\text{g/mol}} = 7.077\,\frac{molLiCl}{s}$$

$$\frac{1.7\text{kg}(1000\text{g/kg})}{18.015\text{g/mol}} = 94.366\,\frac{molH_2O}{s}$$

$$so \quad \tilde{n} = \frac{\text{mols H2O}}{\text{mols solute}} = \frac{94.366}{7.077} = 13.33$$

From Fig 12.14,

$$\Delta\tilde{H}_{\text{mix}} = -33800\,\frac{J}{molSolute}$$

$$\Delta\dot{H}_a^t = 7.077\,\frac{molSolute}{s}(-\Delta\tilde{H}_{\text{mix}})\frac{J}{molSolute} = 239{,}250\,J/s$$

$\Delta\dot{H}_b^t$: Mixing process

Mole entering,

$$\frac{0.03\text{kg}(1000\text{g/kg})}{42.39\text{g/mol}} = 7.077\,\frac{molLiCl}{s}$$

$$\frac{0.45\text{kg}(1000\text{g/kg})}{18.015\text{g/mol}} = 24.98\,\frac{molH_2O}{s}$$

$$so \quad \tilde{n} = \frac{\text{mols H2O}}{\text{mols solute}} = \frac{24.98}{7.077} = 3.53$$

From Fig 12.14,

$$\Delta\tilde{H}_{mix} = -23260\,\frac{J}{molSolute}$$

$$\Delta\dot{H}_a^t = 7.077\,\frac{molSolute}{s}(\Delta\tilde{H}_{mix})\frac{J}{molSolute} = -164630\,J/s$$

$\Delta\dot{H}_c^t$: Heating the solution (Sensible heat),

we need heat capacity data for the solution!!.

$$\Delta\dot{H}_c^t = \dot{m}C_p\Delta T = 0.75\,\tfrac{kg}{s}\left(2.72\,\frac{kJ}{kg^oC}\right)(132-25)^oC$$

$$\Delta\dot{H}_c^t = 218.28\,\tfrac{kJ}{s} = 218280\,\tfrac{J}{s}$$

$\Delta\dot{H}_d^t$: Heating liquid water untill it becomes superheated water

Using steam table

Interpolation

$$\Delta\dot{H}_d^t = \dot{m}\Delta H = \dot{m}(H_{out} - H_{in}) = 1.25\,\tfrac{kg}{s}(2740.3\text{-}104.8\,\tfrac{kJ}{kg})$$

$$\Delta\dot{H}_d^t = 3294.4\,\tfrac{kJ}{s} = 3294400\,\tfrac{J}{s}$$

Use Sat Liq
at 25C

or

Use Riedel

$$\Delta\dot{H}_d^t = \dot{m}\Delta H = \dot{m}(\Delta H_{25\text{-}100C} + \Delta H^n + \Delta H_{100\text{-}132C})$$

Sensible heat

So,

$$\dot{Q} = \Delta\dot{H}^t_a + \Delta\dot{H}^t_b + \Delta\dot{H}^t_c + \Delta\dot{H}^t_d$$

$$\dot{Q} = 239250\text{-}164630 + 218280 + 3294300$$

$$\dot{Q} = 3587300\text{J}$$

$$\dot{Q} = 3587.3 \text{ kJs}^{-1}$$

The rate of heat supply (heat duty) needed to concentrate the solution in the evaporator.

Thank You