Thermodynamics II

Solution Thermodynamics: Applications

Chapter 12

Vapor-Liquid equilibria

From Chapter 11:

- Fugacity
  - For species *i* in the vapor mixture: $\boxed{\hat{f}_i^{\,v} = y_i \hat{\phi}_i^{\,v} P}$
  - Vapor/liquid equilibrium: $\boxed{\mu_i^v = \mu_i^l} \xrightarrow{\boxed{\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i}} \boxed{\hat{f}_i^{\,v} = \hat{f}_i^{\,l}}$
  - The vapor phase is assumed an ideal gas: $\boxed{\hat{\phi}_i^{\,v} = 1}$
  - Therefore: $\boxed{\hat{f}_i^{\,v} = \hat{f}_i^{\,l} = y_i P}$
    - The fugacity of species *i* (in both the liquid and vapor phases) is equal to the partial pressure of species *i* in the vapor phase.

Raoult's law from fugacity phase equilibria (ideal vapor; ideal liquid)

- For species *i* in the ideal vapor phase ($\hat{\phi}_i^v = 1$): $\boxed{\hat{f}_i^{\,v} = y_i \hat{\phi}_i^v P = y_i P}$
- For species *i* in the ideal liquid solution: $\boxed{\hat{f}_i^{\,l} = \hat{f}_i^{\,id} = f_i \; x_i}$
- Fugacity of pure liquid species: $\boxed{f_i = \phi_i^{sat} P_i^{sat} \exp \dfrac{V_i^l (P - P_i^{sat})}{RT}}$

Except for high pressure, the exponential term is closed to unity: $\boxed{f_i = P_i^{sat}}$

$$\boxed{f_i = P_i^{sat}} \longrightarrow \boxed{\hat{f}_i^{\,l} = x_i P_i^{sat}}$$

- Vapor/liquid equilibrium: $\boxed{\hat{f}_i^{\,v} = \hat{f}_i^{\,l}}$

$$\boxed{\hat{f}_i^{\,v} = y_i P} \qquad \boxed{\hat{f}_i^{\,l} = x_i P_i^{sat}}$$

$$\boxed{\hat{f}_i^{\,v} = \hat{f}_i^{\,l}} \longrightarrow \boxed{y_i P = x_i P_i^{sat}}$$

Raoult's law

Modified Raoult's law from fugacity phase equilibria (ideal vapor; non-ideal liquid)

- For species *i* in the ideal vapor phase ($\hat{\phi}_i^v = 1$): $\boxed{\hat{f}_i^{\,v} = y_i \hat{\phi}_i^v P = y_i P}$
- For species *i* in the real liquid solution: $\boxed{\hat{f}_i^{\,l} = \gamma_i f_i \; x_i}$
- Fugacity of pure liquid species: $\boxed{f_i = \phi_i^{sat} P_i^{sat} \exp \dfrac{V_i^l (P - P_i^{sat})}{RT}}$

Except for high pressure, the exponential term is closed to unity: $\boxed{f_i = P_i^{sat}}$

$$\boxed{f_i = P_i^{sat}} \;\downarrow\; \boxed{\hat{f}_i^{\,l} = \gamma_i x_i P_i^{sat}}$$

- Vapor/liquid equilibrium: $\boxed{\hat{f}_i^{\,v} = \hat{f}_i^{\,l}}$

$$\boxed{\hat{f}_i^{\,v} = y_i P} \quad \boxed{\hat{f}_i^{\,l} = \gamma_i x_i P_i^{sat}}$$

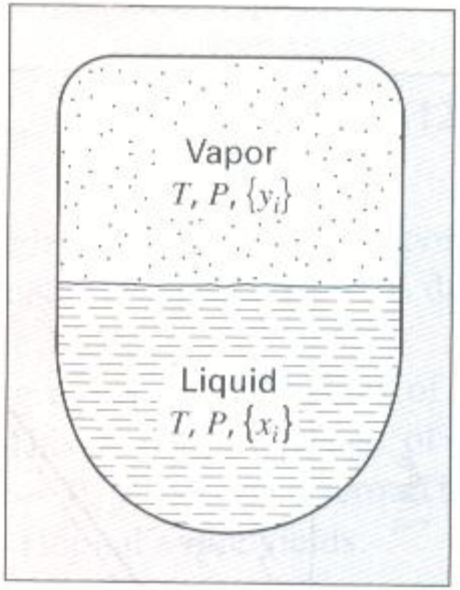
$$\downarrow$$

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

Modified Raoult's law

Fugacity and activity coefficients from VLE experiments:

Fig. 12.1



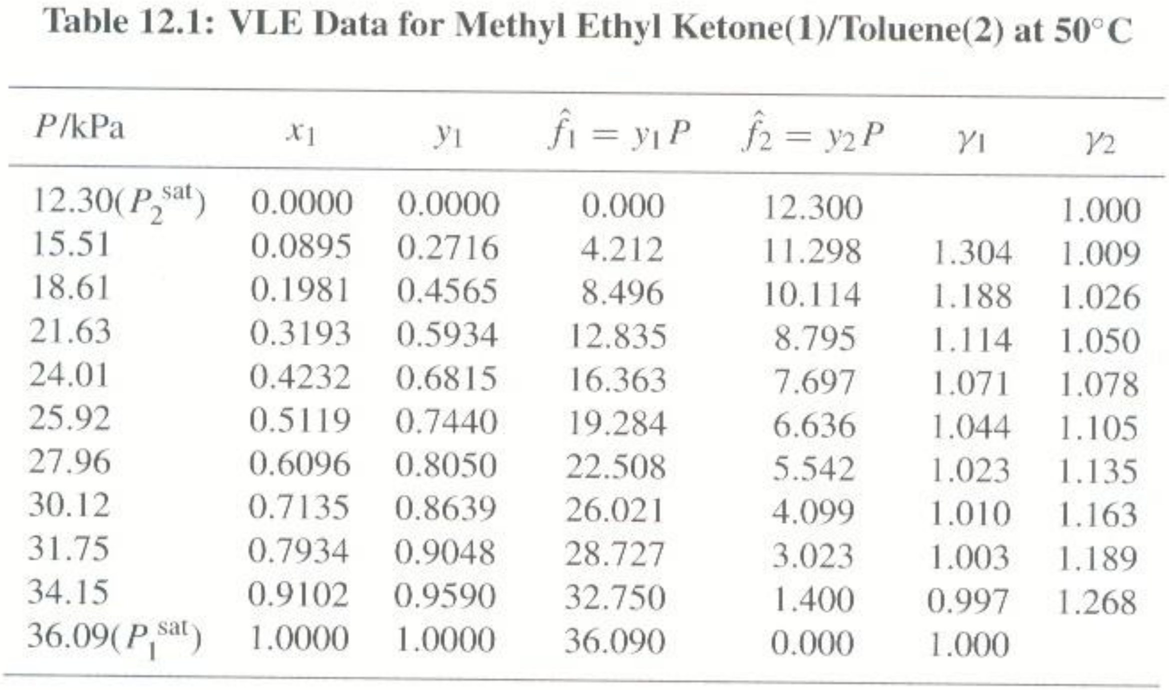


Table 12.1: VLE Data for Methyl Ethyl Ketone(1)/Toluene(2) at 50°C

P/kPa	x_1	y_1	$\hat{f}_1 = y_1 P$	$\hat{f}_2 = y_2 P$	γ_1	γ_2
12.30(P_2^{sat})	0.0000	0.0000	0.000	12.300		1.000
15.51	0.0895	0.2716	4.212	11.298	1.304	1.009
18.61	0.1981	0.4565	8.496	10.114	1.188	1.026
21.63	0.3193	0.5934	12.835	8.795	1.114	1.050
24.01	0.4232	0.6815	16.363	7.697	1.071	1.078
25.92	0.5119	0.7440	19.284	6.636	1.044	1.105
27.96	0.6096	0.8050	22.508	5.542	1.023	1.135
30.12	0.7135	0.8639	26.021	4.099	1.010	1.163
31.75	0.7934	0.9048	28.727	3.023	1.003	1.189
34.15	0.9102	0.9590	32.750	1.400	0.997	1.268
36.09(P_1^{sat})	1.0000	1.0000	36.090	0.000	1.000	

- The first three columns are P-x_1-y_1 experimental data.
- Columns 4 and 5 are calculated from : $\boxed{\hat{f}_1 = y_1 P}$ $\boxed{\hat{f}_2 = y_2 P}$
- Column 6 is: $\boxed{\gamma_1 = y_1 P / (x_1 P_1^{sat})}$
- Column 7 is: $\boxed{\gamma_2 = y_2 P / (x_2 P_2^{sat})}$

$$\boxed{\begin{aligned} y_2 &= 1 - y_1 \\ x_2 &= 1 - x_1 \end{aligned}}$$

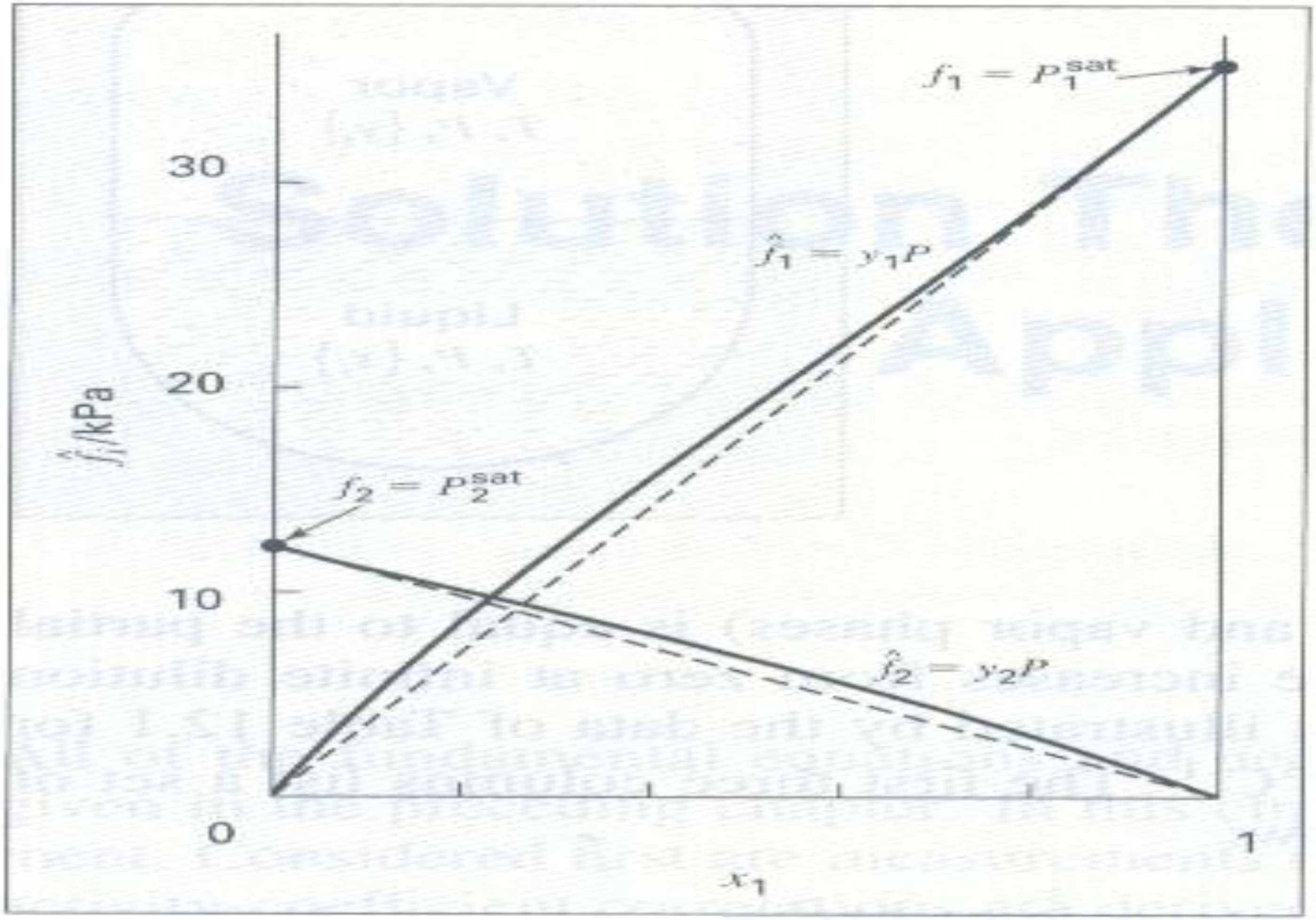


Figure 12.2 Fugacities for methyl ethyl ketone(1)/toluene(2) at 323.15 K (50°C). The dashed lines represent the Lewis/Randall rule

When $x_i \rightarrow 0: \hat{f}_i \rightarrow 0$

When $x_i \rightarrow 1: \hat{f}_i \rightarrow P_i^{sat}$

Species fugacity value increases from zero to P_i^{sat} for pure species *i*

Henry's law from fugacity phase equilibria (ideal vapor; infinite dilution: $x_i \to 0$)

$$\lim_{x_i \to 0} \frac{\hat{f}_i}{x_i} = \frac{0}{0}: \text{ Indeterminate ratio}$$

- To determine such ratio, use L'Hospital's Rule to have: $\lim_{x_i \to 0} \frac{\hat{f}_i}{x_i} = \left(\frac{d\hat{f}_i}{dx_i} \right)_{x_i = 0}$

Thus, for infinite dilution of species i:

$$\boxed{\frac{\hat{f}_i}{x_i} = \text{The limiting slope of the } \hat{f}_i \text{ } vs. x_i \text{ curve at } x_i = 0}$$

It is found that such limiting slope is exactly equals to Henry’s constant:

$$\boxed{x_i \to 0: \frac{\hat{f}_i}{x_i} \equiv H_i} \to \boxed{\hat{f}_i = y_i P = H_i x_i}$$ **Henry's law**

Henry's law from fugacity phase equilibria (ideal vapor; infinite dilution: $x_i \rightarrow 0$)

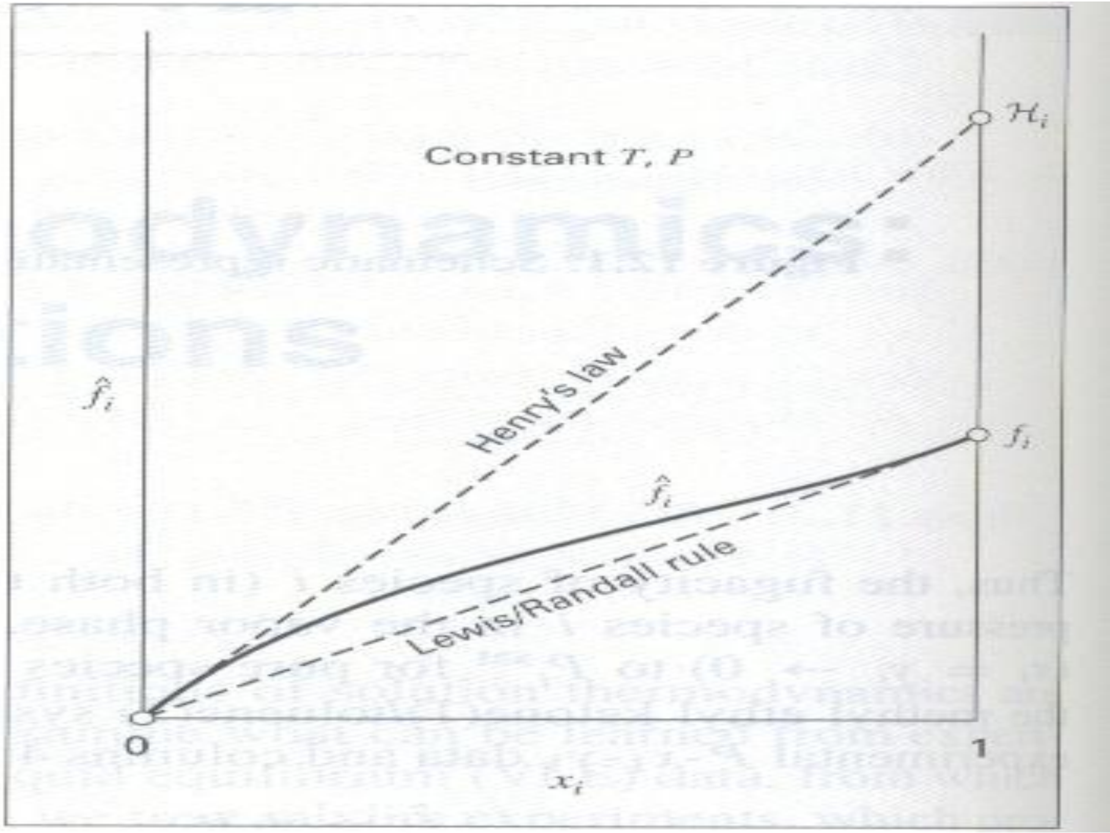


Figure 12.3 Composition dependence of fugacity for species i in a binary solution

$$\boxed{\text{Henry's law}} \xrightarrow{\boxed{\text{Gibbs/Duhem equation}}} \boxed{\text{Lewis/Randall rule}}$$

$x_1 \to 0$ $x_1 \to 1$

Gibbs/Duhem equation for binary mixture at const. T and P: $\boxed{x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0}$

$$\boxed{\bar{M}_i = \bar{G}_i = \mu_i}$$

$$\boxed{x_1 d\mu_1 + x_2 d\mu_2 = 0}$$

$$\boxed{d\mu_i = RT \ln \hat{f}_i}$$

$$\boxed{x_1 d \ln \hat{f}_1 + x_2 d \ln \hat{f}_2 = 0}$$

Division by dx_1

$$\boxed{x_1 \frac{d \ln \hat{f}_1}{dx_1} + x_2 \frac{d \ln \hat{f}_2}{dx_1} = 0}$$

$$\boxed{dx_1 + dx_2 = 0}$$

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

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

limit

$$\boxed{\lim_{x_1 \to 1} \frac{d\hat{f}_1 / dx_1}{\hat{f}_1 / x_1} = \lim_{x_2 \to 0} \frac{d\hat{f}_2 / dx_2}{\hat{f}_2 / x_2}}$$

when $x_1 = 1$, $\boxed{\hat{f}_1 = f_1}$

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

$$\boxed{\frac{1}{f_1}\left(\frac{d\hat{f}_1}{dx_1}\right)_{x_1=1} = \frac{H_2}{H_2} = 1}$$

$$\boxed{\left(\frac{d\hat{f}_1}{dx_1}\right)_{x_1=1} = f_1}$$

The Lewis/Randall rule,

$$\boxed{\left(\hat{f}_i \approx \hat{f}_i^{\,id} = x_i f_i\right)_{x_i \approx 1}}$$

Data reduction

- Data reduction: replacing the VLE data by an equation for excess Gibbs energy through curve fitting using an appropriate model.

weak

- G^E/RT = f (T, P, composition): $$\boxed{\frac{G^E}{RT} = g\left(T, x_1, x_2, \ldots, x_N\right)}$$

-At constant T: $$\boxed{\frac{G^E}{RT} = g\left(x_1, x_2, \ldots, x_N\right)}$$

- Models for data reduction: Margules, Van Laar, NRTL, Wilson, UNIQUAC, UNIFAC, ..etc.
- Then:

$$\boxed{\ln\gamma_i = \left[\frac{\partial\left(nG^E/RT\right)}{\partial n_i}\right]_{P,T,n_j}}$$

$$\boxed{P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat}}$$

$$\boxed{\begin{aligned} y_1 &= x_1\gamma_1P_1^{sat}/P \\ y_2 &= x_2\gamma_2P_2^{sat}/P \end{aligned}}$$

Data reduction

Redlich/Kister expansion (binary system):

$$\boxed{\frac{G^E}{x_1x_2RT} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots}$$

- If B = C =…..= 0: $\boxed{\frac{G^E}{x_1x_2RT} = A}$ **Two-suffix Margules equation**

$$\downarrow$$

$$\boxed{\frac{G^E}{RT} = Ax_1x_2} \longrightarrow \boxed{\frac{nG^E}{RT} = A\frac{n_1n_2}{(n_1+n_2)^2}}$$

$$\downarrow$$

$$\boxed{\ln\gamma_1 = \left[\frac{\partial\left(nG^E/RT\right)}{\partial n_1}\right]_{P,T,n_2} = Ax_2^2} \qquad \boxed{\ln\gamma_2 = \left[\frac{\partial\left(nG^E/RT\right)}{\partial n_2}\right]_{P,T,n_1} = Ax_1^2}$$

The infinite dilution values of activity coefficients are:

$$\boxed{\ln\gamma_1^\infty|_{x_1=0} = A \qquad \ln\gamma_2^\infty|_{x_2=0} = A}$$

- If two-suffix Margules model is valid, $G^E/(x_1x_2RT)$ must NOT vary with composition.

Data reduction

Redlich/Kister expansion (binary system):

- If C =D…..= 0:

$$\boxed{\frac{G^E}{x_1x_2RT} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots}$$

$$\boxed{\frac{G^E}{x_1x_2RT} = A + B(x_1 - x_2)}$$

$$\boxed{A - B = A_{12}} \qquad \boxed{A + B = A_{21}}$$

Three-suffix Margules equation

$$\boxed{\frac{G^E}{x_1x_2RT} = A_{21}x_1 + A_{12}x_2}$$

$$\boxed{\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2} \longrightarrow \boxed{\frac{nG^E}{RT} = (A_{21}n_1 + A_{12}n_2)\frac{n_1n_2}{(n_1 + n_2)^2}}$$

$$\boxed{\ln\gamma_1 = \left[\frac{\partial\left(nG^E/RT\right)}{\partial n_1}\right]_{P,T,n_2} = x_2\left[(A_{21}x_1 + A_{12}x_2)(1 - 2x_1) + A_{21}x_1\right] = x_2^2\left[A_{12} + 2(A_{21} - A_{12})x_1\right]}$$

Similarly, $\boxed{\ln\gamma_2 = x_1^2\left[A_{21} + 2(A_{12} - A_{21})x_2\right]}$ and $\boxed{\ln\gamma_1^\infty|_{x_1=0} = A_{12}}$ $\boxed{\ln\gamma_2^\infty|_{x_2=0} = A_{21}}$

- If three-suffix Margules model is valid, $G^E/(x_1x_2RT)$ must varies linearly with x_1 or x_2.

Data reduction

Example. Do you think that VLE data for Methyl Ethyl ketone (1) / Toluene (2) at 50 °C given below can be reduced using two- or three-suffix Margules equation why? If yes find it parameters A12 and A21.

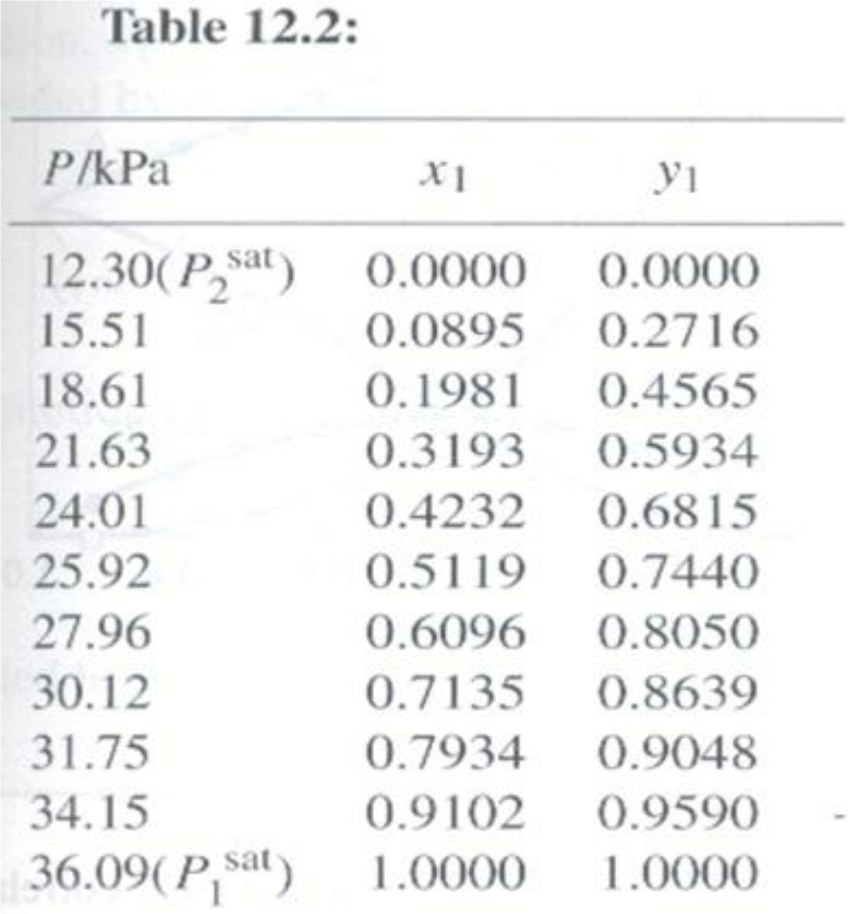


Table 12.2:

P/kPa	x_1	y_1
12.30(P_2^{sat})	0.0000	0.0000
15.51	0.0895	0.2716
18.61	0.1981	0.4565
21.63	0.3193	0.5934
24.01	0.4232	0.6815
25.92	0.5119	0.7440
27.96	0.6096	0.8050
30.12	0.7135	0.8639
31.75	0.7934	0.9048
34.15	0.9102	0.9590
36.09(P_1^{sat})	1.0000	1.0000

Data reduction

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

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

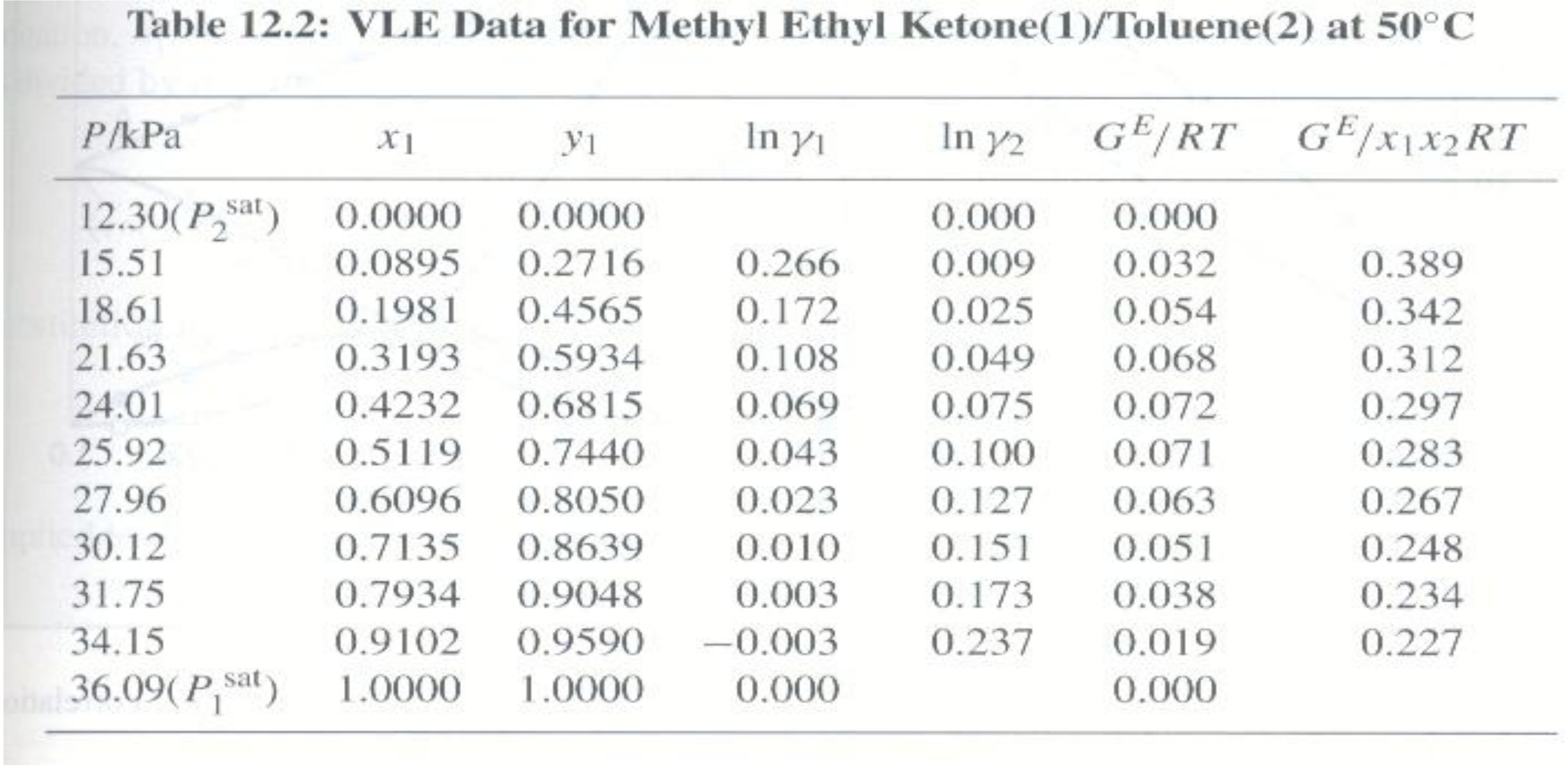


Table 12.2: VLE Data for Methyl Ethyl Ketone(1)/Toluene(2) at 50°C

P/kPa	x_1	y_1	$\ln \gamma_1$	$\ln \gamma_2$	G^E/RT	G^E/x_1x_2RT
12.30(P_2^{sat})	0.0000	0.0000		0.000	0.000	
15.51	0.0895	0.2716	0.266	0.009	0.032	0.389
18.61	0.1981	0.4565	0.172	0.025	0.054	0.342
21.63	0.3193	0.5934	0.108	0.049	0.068	0.312
24.01	0.4232	0.6815	0.069	0.075	0.072	0.297
25.92	0.5119	0.7440	0.043	0.100	0.071	0.283
27.96	0.6096	0.8050	0.023	0.127	0.063	0.267
30.12	0.7135	0.8639	0.010	0.151	0.051	0.248
31.75	0.7934	0.9048	0.003	0.173	0.038	0.234
34.15	0.9102	0.9590	−0.003	0.237	0.019	0.227
36.09(P_1^{sat})	1.0000	1.0000	0.000		0.000	

Data reduction

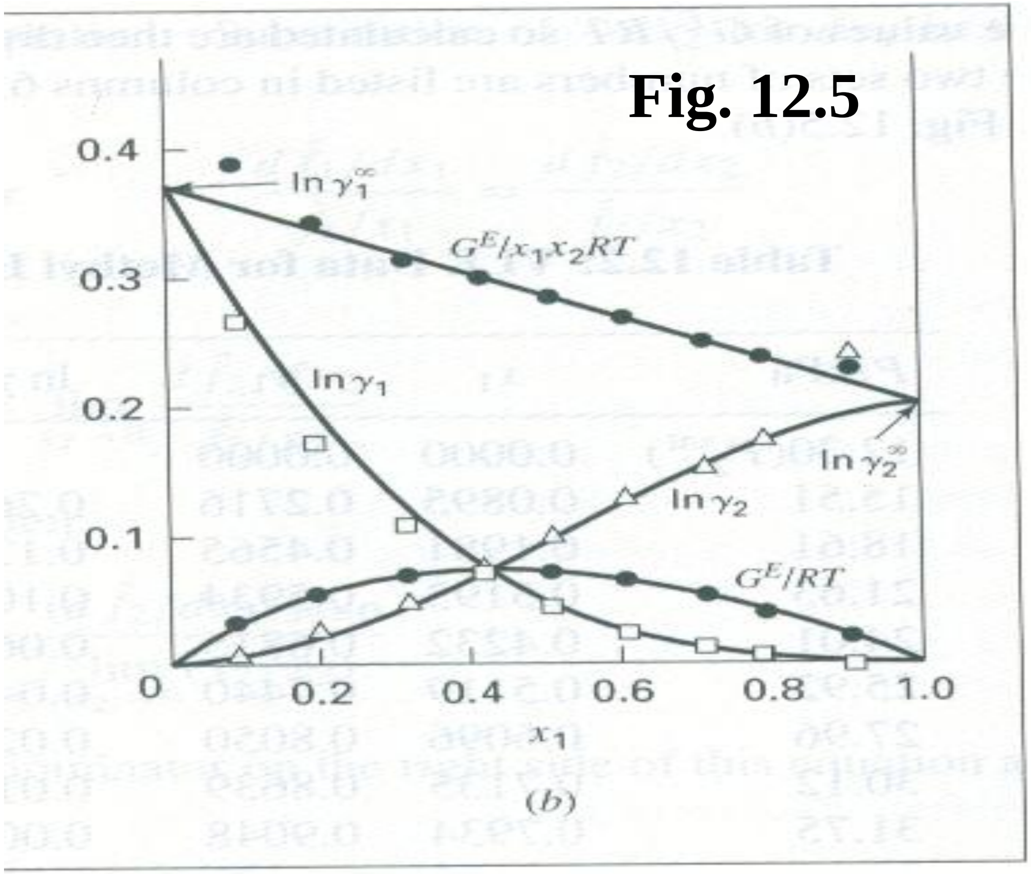


Fig. 12.5

The value of G^E/RT is zero at both x_1= 0 and x_1 =1:

$$\boxed{\lim_{x_1\to 0}\frac{G^E}{RT} = (0)\ln\gamma_1^\infty + (1)(0) = 0}$$

$$\boxed{\lim_{x_2\to 0}\frac{G^E}{RT} = (1)(0) + (0)(\ln\gamma_2^\infty) = 0}$$

- Yes, Margules model is valid for data reduction since $G^E/(x_1x_2RT)$ varies linearly with x_1.

$$\boxed{\lim_{x_1\to 0}\frac{G^E}{x_1x_2RT} = \ln\gamma_1^\infty = A_{12} = 0.372} \qquad \boxed{\lim_{x_1\to 1}\frac{G^E}{x_1x_2RT} = \ln\gamma_2^\infty = A_{21} = 0.198}$$

Data reduction

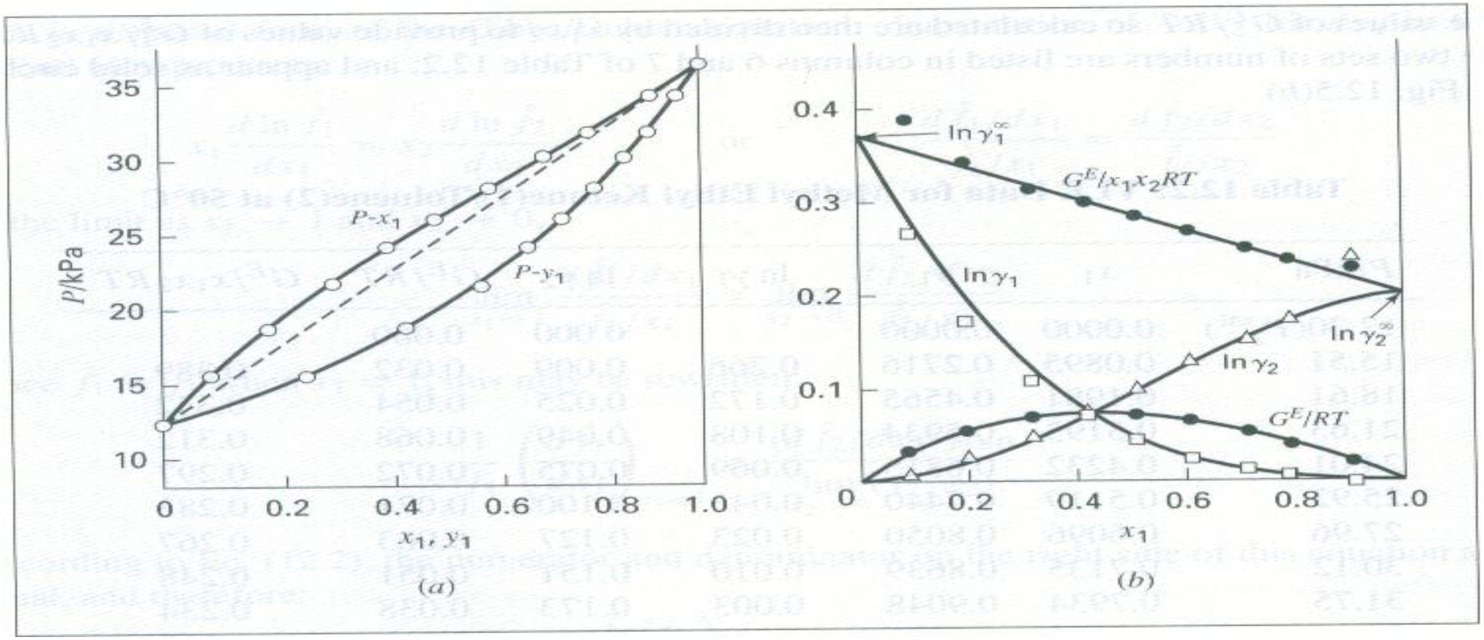


Fig. 12.5

$$\boxed{\ln \gamma_i \geq 0} \longrightarrow \boxed{\gamma_i \geq 1}$$

$$\downarrow$$

It means positive deviation from Raoult's law behavior.

Data reduction

van Laar Model: $$\boxed{\frac{G^E}{x_1x_2RT}=\frac{A'_{12}+A'_{21}}{A'_{12}x_1+A'_{21}x_2}}$$ (Two parameters model)

$$\downarrow$$

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

$$\downarrow$$

$$\boxed{\frac{nG^E}{RT}=\left(A_{21}n_1+A_{12}n_2\right)\frac{n_1n_2}{(n_1+n_2)^2}}$$

$$\downarrow$$

$$\boxed{\ln\gamma_1=\left[\frac{\partial\left(nG^E/RT\right)}{\partial n_1}\right]_{P,T,n_2}=A'_{12}\left(1+\frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2}}$$

$$\boxed{\ln\gamma_2=\left[\frac{\partial\left(nG^E/RT\right)}{\partial n_2}\right]_{P,T,n_1}=A'_{21}\left(1+\frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2}}$$

$$\boxed{\ln\gamma_1^\infty|_{x_1=0}=A'_{12}}$$

$$\boxed{\ln\gamma_2^\infty|_{x_2=0}=A'_{21}}$$

- If van Laar Margules model is valid, x_1x_2RT/G^E must varies linearly with x_1 or x_2.

Data reduction

Non-Random-Two-Liquid (NRTL) Model :

$$\boxed{\frac{G^E}{x_1x_2RT} = \frac{G_{21}\tau_{21}}{x_1 + x_2G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1G_{12}}}$$

(Three parameters model)

$$G_{12} = \exp(-\alpha\tau_{12}) \qquad G_{21} = \exp(-\alpha\tau_{21})$$

$$\tau_{12} = \frac{b_{12}}{RT} \qquad \tau_{21} = \frac{b_{21}}{RT}$$

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{(x_2 + x_1G_{12})^2}\right]$$

$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{(x_1 + x_2G_{21})^2}\right]$$

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

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

Data reduction

Wilson Model:

Multicomponent system:

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

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

(Two parameters model)

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp \frac{-a_{ij}}{RT} \qquad (i \neq j) \qquad \Lambda_{ij} = 1 \text{ for } i = j \qquad \Lambda_{ij} \neq \Lambda_{ji}$$

V_i : molar volumes of pure species i

V_j : molar volumes of pure species j

Data reduction

Wilson Model:

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

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

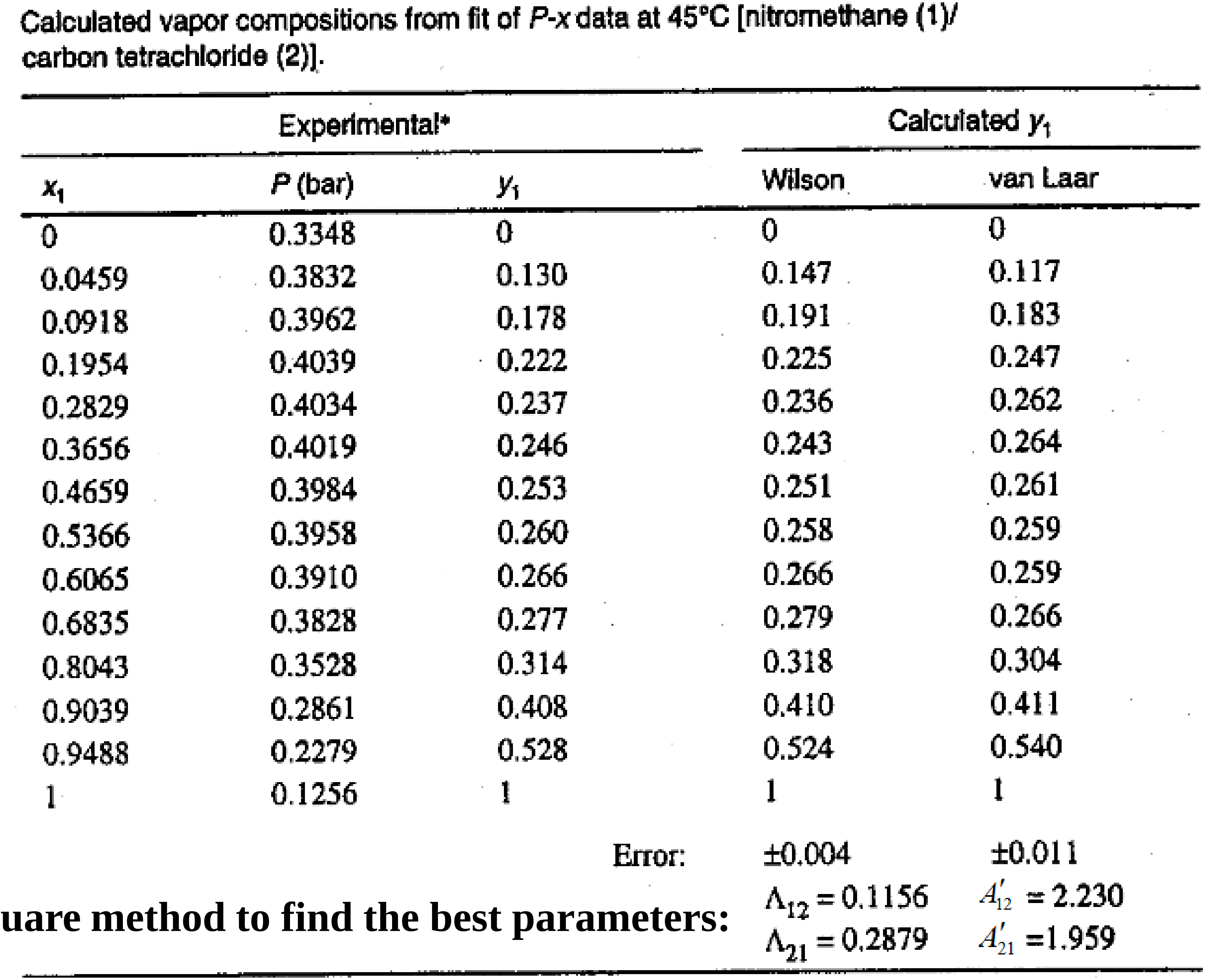
$$\ln \gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) - x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)$$

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

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

- The **UNIQUAC** (UNIversal QUAsi-Chemical) and **UNIFAC** ((**UNI**QUAC **F**unctional-group **A**ctivity **C**oefficients) models are of greater complexity and are treated in App. H.

Data reduction

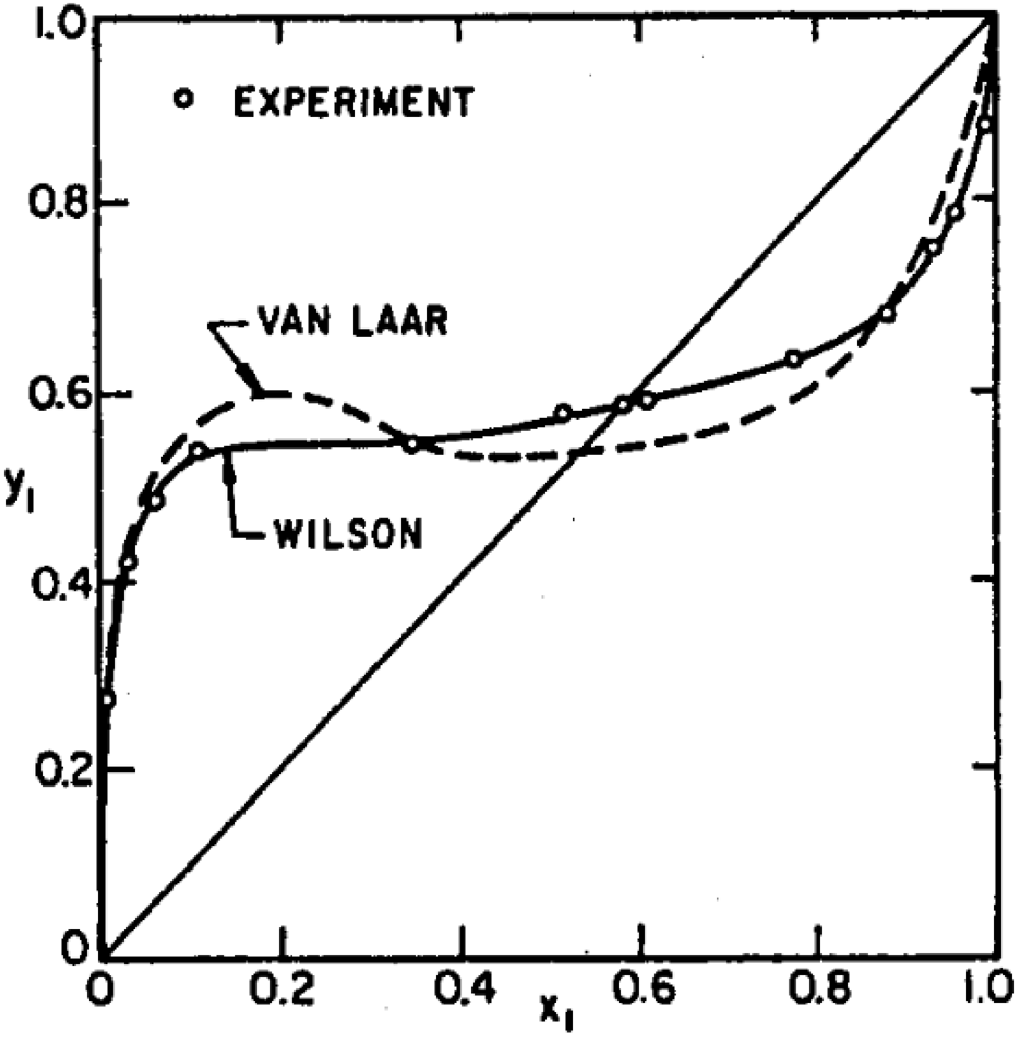


Calculated vapor compositions from fit of *P*-*x* data at 45°C [nitromethane (1)/ carbon tetrachloride (2)].

Experimental*			Calculated y_1	
x_1	P (bar)	y_1	Wilson	van Laar
0	0.3348	0	0	0
0.0459	0.3832	0.130	0.147	0.117
0.0918	0.3962	0.178	0.191	0.183
0.1954	0.4039	0.222	0.225	0.247
0.2829	0.4034	0.237	0.236	0.262
0.3656	0.4019	0.246	0.243	0.264
0.4659	0.3984	0.253	0.251	0.261
0.5366	0.3958	0.260	0.258	0.259
0.6065	0.3910	0.266	0.266	0.259
0.6835	0.3828	0.277	0.279	0.266
0.8043	0.3528	0.314	0.318	0.304
0.9039	0.2861	0.408	0.410	0.411
0.9488	0.2279	0.528	0.524	0.540
1	0.1256	1	1	1
		Error:	±0.004	±0.011
			$\Lambda_{12} = 0.1156$ $\Lambda_{21} = 0.2879$	$A'_{12} = 2.230$ $A'_{21} = 1.959$

Least-square method to find the best parameters:

Data reduction



Vapor-liquid equilibrium for the ethanol (1)/ isooctane (2) system at 50°C. Lines calculated from *P-x* data.

Thermodynamic consistency

- Testing experimental VLE data for thermodynamic consistency”
- General rule: If the VLE data do NOT obey Gibbs/Duhem equation, the data can NOT be consistent “correct
- Thus, all consistency tests are based on Gibbs/Duhem equation (constant T and P):

Binary system:

$$\boxed{\sum x_i d\ln\gamma_i = 0} \longrightarrow \boxed{x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0}$$

- Examples of consistency tests: Integral method, Baker’s method,..etc.

Consistency test

Binary system:

$$G^E/(RT) = \sum x_i \ln \gamma_i = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

Differentiate

$$d\left(G^E/(RT)\right) = x_1 d \ln \gamma_1 + \ln \gamma_1 dx_1 + x_2 d \ln \gamma_2 + \ln \gamma_2 dx_2$$

Equilibrium: constant T and P

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0$$

$$d\left(G^E/(RT)\right) = \ln \gamma_1 dx_1 + \ln \gamma_2 dx_2$$

$$dx_2 = -dx_1$$

$$d\left(\frac{G^E}{RT}\right) = \ln\left(\frac{\gamma_1}{\gamma_1}\right) dx_1$$

Integrate

$$\left.\frac{G^E}{RT}\right|_{at\, x_1=0}^{at\, x_1=1} = \int_{x_1=0}^{1} \ln\left(\frac{\gamma_1}{\gamma_1}\right) dx_1$$

$$\int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_1}\right) dx_1 = 0$$

To have consistent VLE data, the area enclosed between the x_1 axis and $\ln(\gamma_1/\gamma_1)$ must be zero.

Thermodynamic consistency

Example. Use integral method to check the consistency of VLE data for diethyl ketone (1) / n-hexane (2) at 65°C are given in Table 12.4.

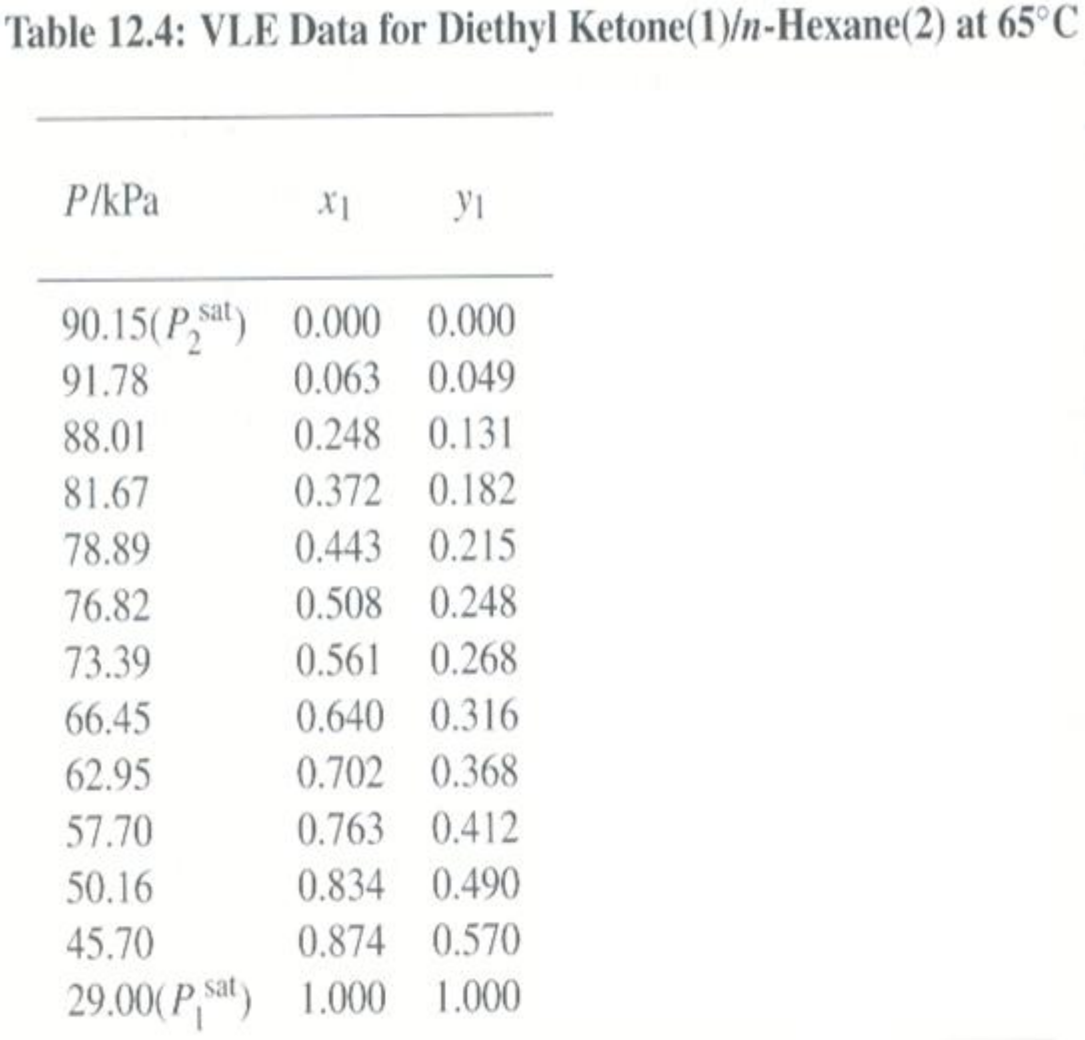


Table 12.4: VLE Data for Diethyl Ketone(1)/*n*-Hexane(2) at 65°C

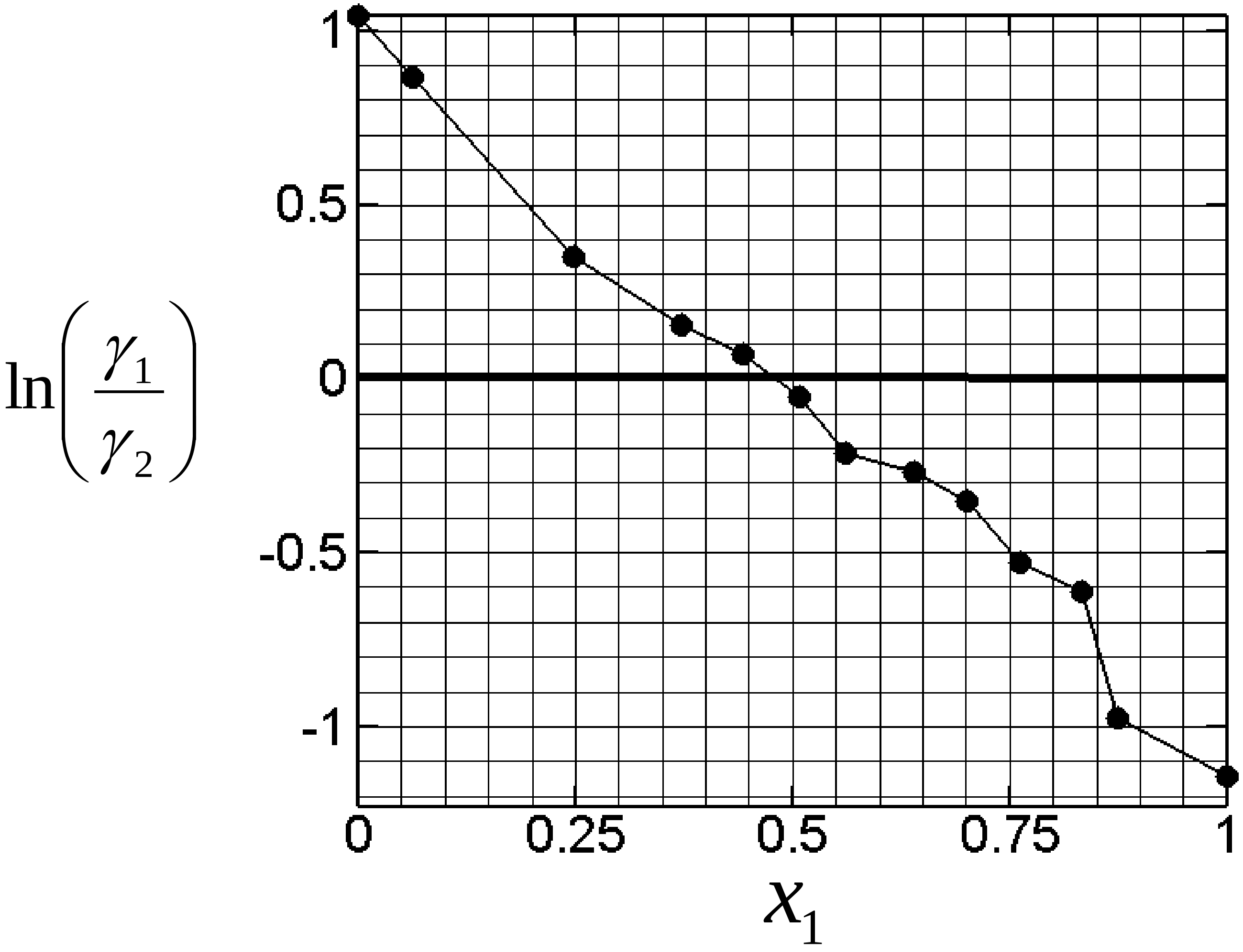
P/kPa	x_1	y_1
90.15(P_2^{sat})	0.000	0.000
91.78	0.063	0.049
88.01	0.248	0.131
81.67	0.372	0.182
78.89	0.443	0.215
76.82	0.508	0.248
73.39	0.561	0.268
66.45	0.640	0.316
62.95	0.702	0.368
57.70	0.763	0.412
50.16	0.834	0.490
45.70	0.874	0.570
29.00(P_1^{sat})	1.000	1.000

Thermodynamic consistency

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

P, kPa	x_1	y_1	γ_1	γ_2	$\ln(\gamma_1/\gamma_2)$
90.1500	0.0000	0.0000	2.7539	1.0000	1.0439
91.7800	0.0630	0.0490	2.4615	1.0333	0.8680
88.0100	0.2480	0.1310	1.6031	1.1282	0.3513
81.6700	0.3720	0.1820	1.3778	1.1800	0.1550
78.8900	0.4430	0.2150	1.3203	1.2333	0.0681
76.8200	0.5080	0.2480	1.2355	1.3025	-0.0528
73.3900	0.5610	0.2680	1.0946	1.3574	-0.2152
66.4500	0.6400	0.3160	1.0718	1.4005	-0.2675
62.9500	0.7020	0.3680	1.0430	1.4809	-0.3506
57.7000	0.7630	0.4120	0.9340	1.5880	-0.5308
50.1600	0.8340	0.4900	0.9259	1.7094	-0.6132
45.7000	0.8740	0.5700	0.6522	1.7300	-0.9756
29.0000	1.0000	1.0000	1.0000	1.8245	-1.1410

Thermodynamic consistency



The area enclosed between the x_1 axis and $\ln(\gamma_1/\gamma_1) \approx -0.082$. Thus the data are NOT consistent.

Thermodynamic consistency

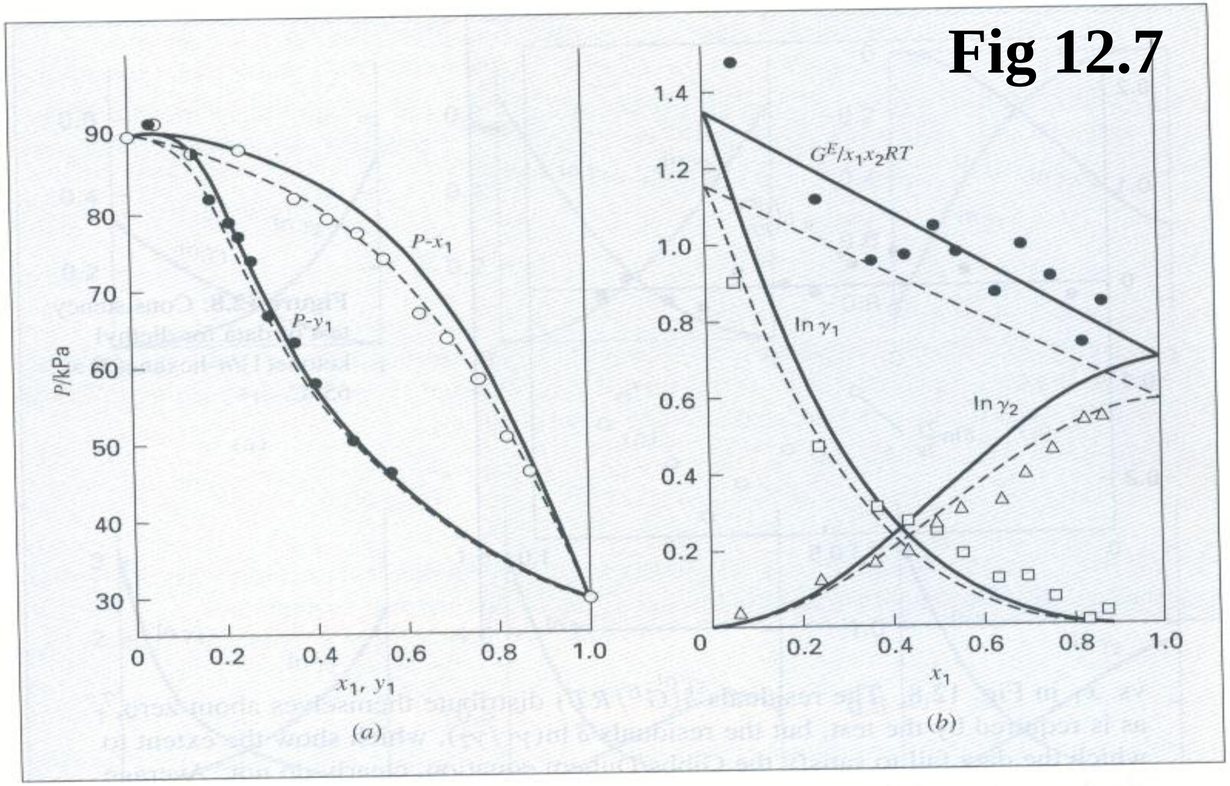


Fig 12.7

Scattering values of $G^E/(x_1x_2RT)$ indicate clearly the experimental data inconsistency.

Property changes of mixing

- Excess properties: $\boxed{M^E = M - M^{id}}$

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

$$\boxed{S^E = S - \sum_i x_i S_i + R \sum_i x_i \ln x_i}$$

$$\boxed{V^E = V - \sum_i x_i V_i}$$

$$\boxed{H^E = H - \sum_i x_i H_i}$$

$$\boxed{\Delta M \equiv M - \sum_i x_i M_i}$$

The M change of mixing

$$\boxed{G^E = \Delta G - RT \sum_i x_i \ln x_i}$$

$$\boxed{S^E = \Delta S + R \sum_i x_i \ln x_i}$$

$$\boxed{V^E = \Delta V}$$

$$\boxed{H^E = \Delta H}$$

- Because of their direct measurability, ΔV and ΔH are the property changes of mixing of major interest.
- G^E and then ΔV can be obtained from VLE experiments.
- S^E and then ΔS can be obtained using: $\boxed{G^E = H^E - TS^E S}$

$$\boxed{S^E = (H^E - G^E)/T}$$

Property changes of mixing

How to measure ΔV and ΔH in the lab?

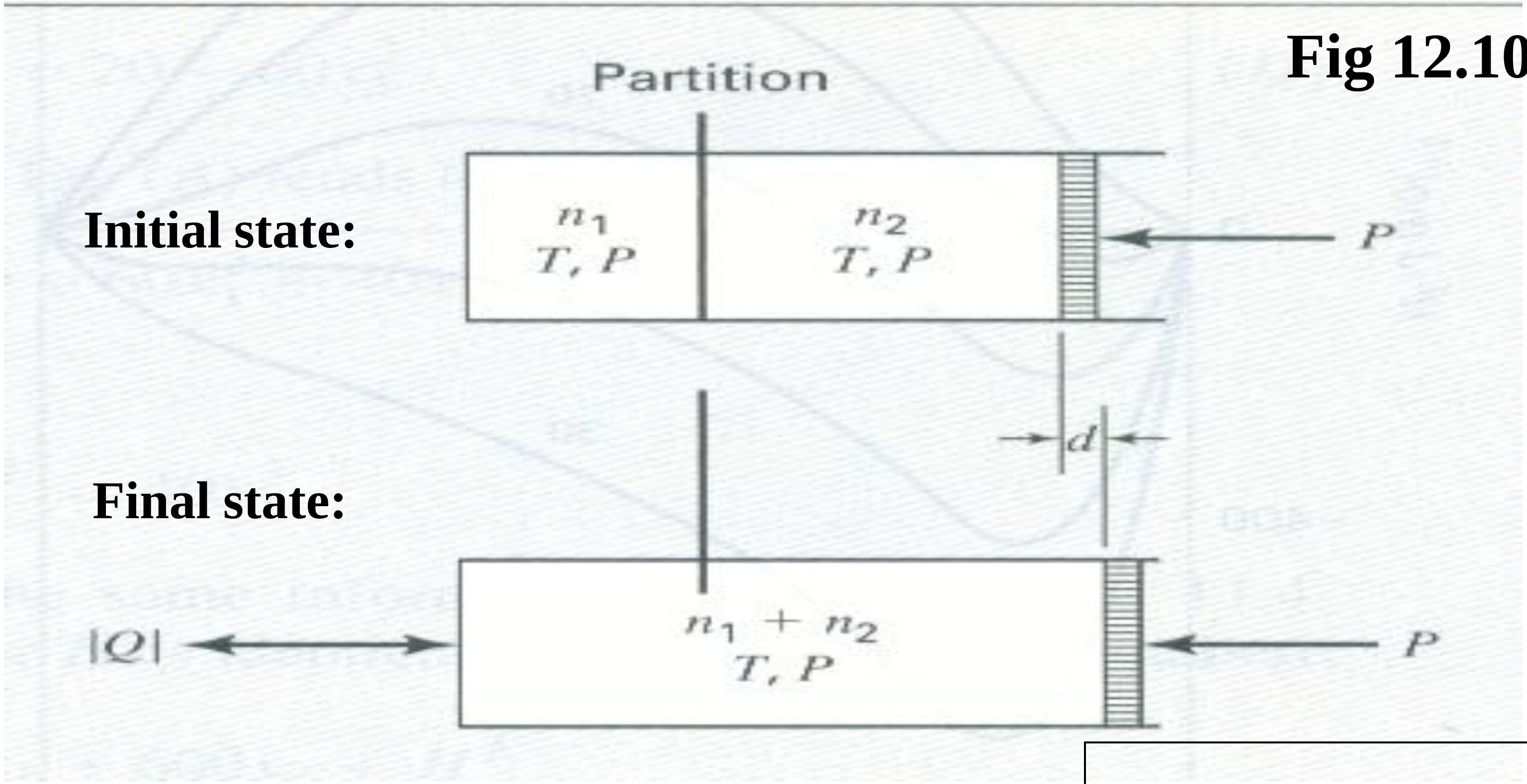


Fig 12.10

Initial state:

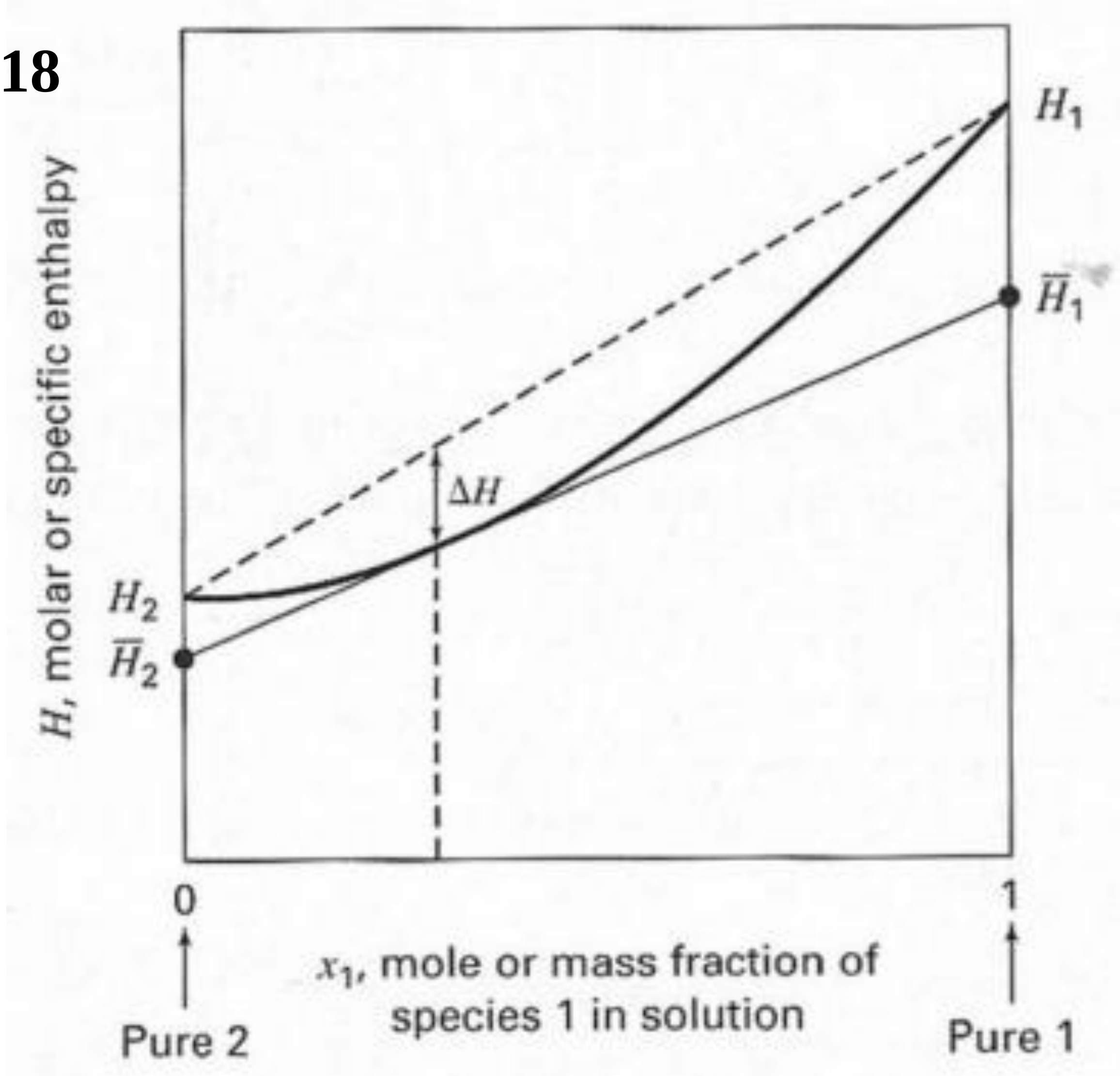
Final state:

$$\boxed{\Delta V^t = (n_1 + n_2)V - n_1V_1 - n_2V_2} \longrightarrow \boxed{\Delta V \equiv V - x_1V_1 - x_2V_2 = \frac{\Delta V^t}{n_1 + n_2}}$$

$$\boxed{Q = \Delta H^t = (n_1 + n_2)H - n_1H_1 - n_2H_2} \longrightarrow \boxed{\Delta H \equiv H - x_1H_1 - x_2H_2 = \frac{Q}{n_1 + n_2}}$$

Property changes of mixing

Fig 12.18



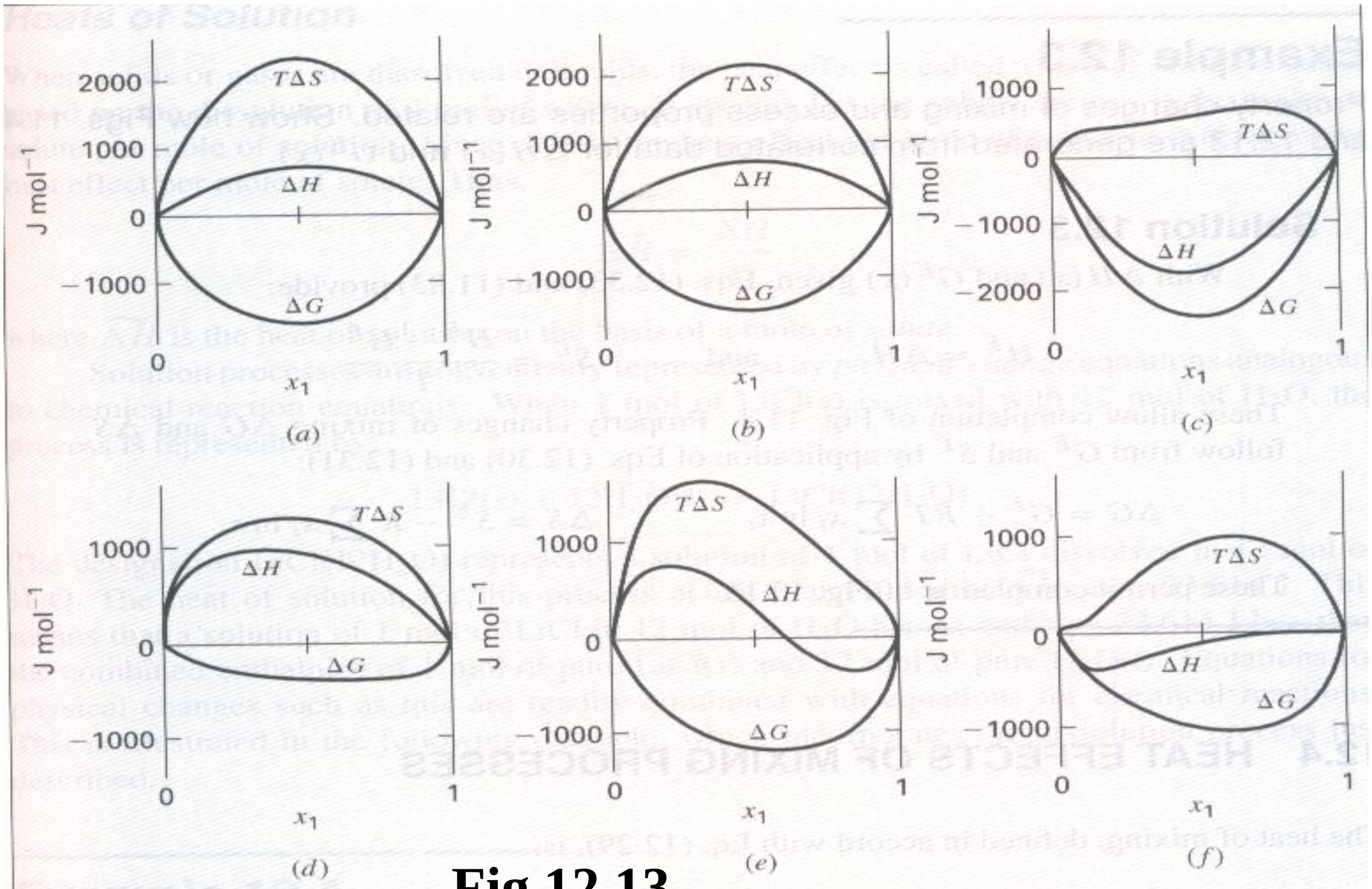


Fig 12.13

1. Each ΔM is zero for a pure species.
2. The Gibbs energy change of mixing ΔG is always negative.
3. The entropy change of mixing ΔS is positive.

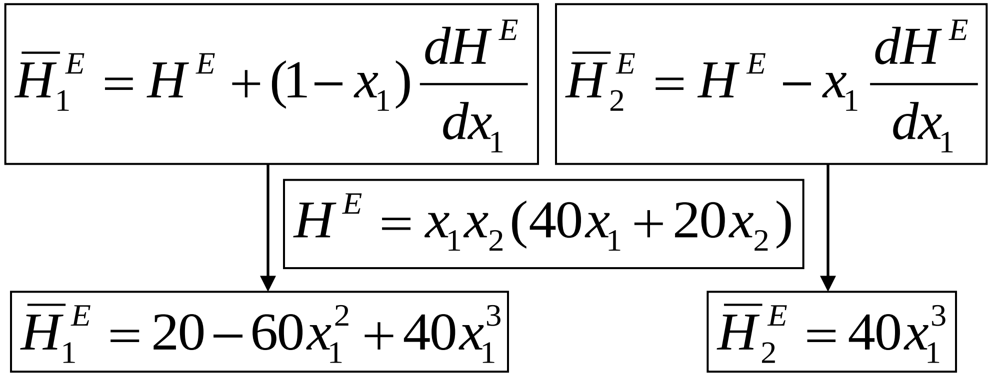
Property changes of mixing

Example 12.2 . The excess enthalpy (heat of mixing) for liquid mixture of species 1 and 2 at fixed T and P is represented by the equation: $H^E = x_1 x_2 (40x_1 + 20x_2)$

Determine expressions for $\bar{H}_1^E$ and $\bar{H}_2^E$ as functions of x_i.

The partial properties:

(Chapter 11)



$$\boxed{\bar{H}_1^E = H^E + (1 - x_1)\frac{dH^E}{dx_1}}$$

$$\boxed{\bar{H}_2^E = H^E - x_1 \frac{dH^E}{dx_1}}$$

$$\boxed{H^E = x_1 x_2 (40x_1 + 20x_2)}$$

$$\boxed{\bar{H}_1^E = 20 - 60x_1^2 + 40x_1^3}$$

$$\boxed{\bar{H}_2^E = 40x_1^3}$$

Heat of mixing and heat of solution

- Heat of mixing: $\boxed{\Delta H = H - \sum_i x_i H_i}$
  - For binary systems: $\boxed{H = x_1 H_1 + x_2 H_2 + \Delta H}$
  - When a mixture is formed, a similar energy change occurs because interactions between the force fields of like and unlike molecules are different.
- **Heat of solution**
  - based on *1 mol* of solute dissolve in liquids:

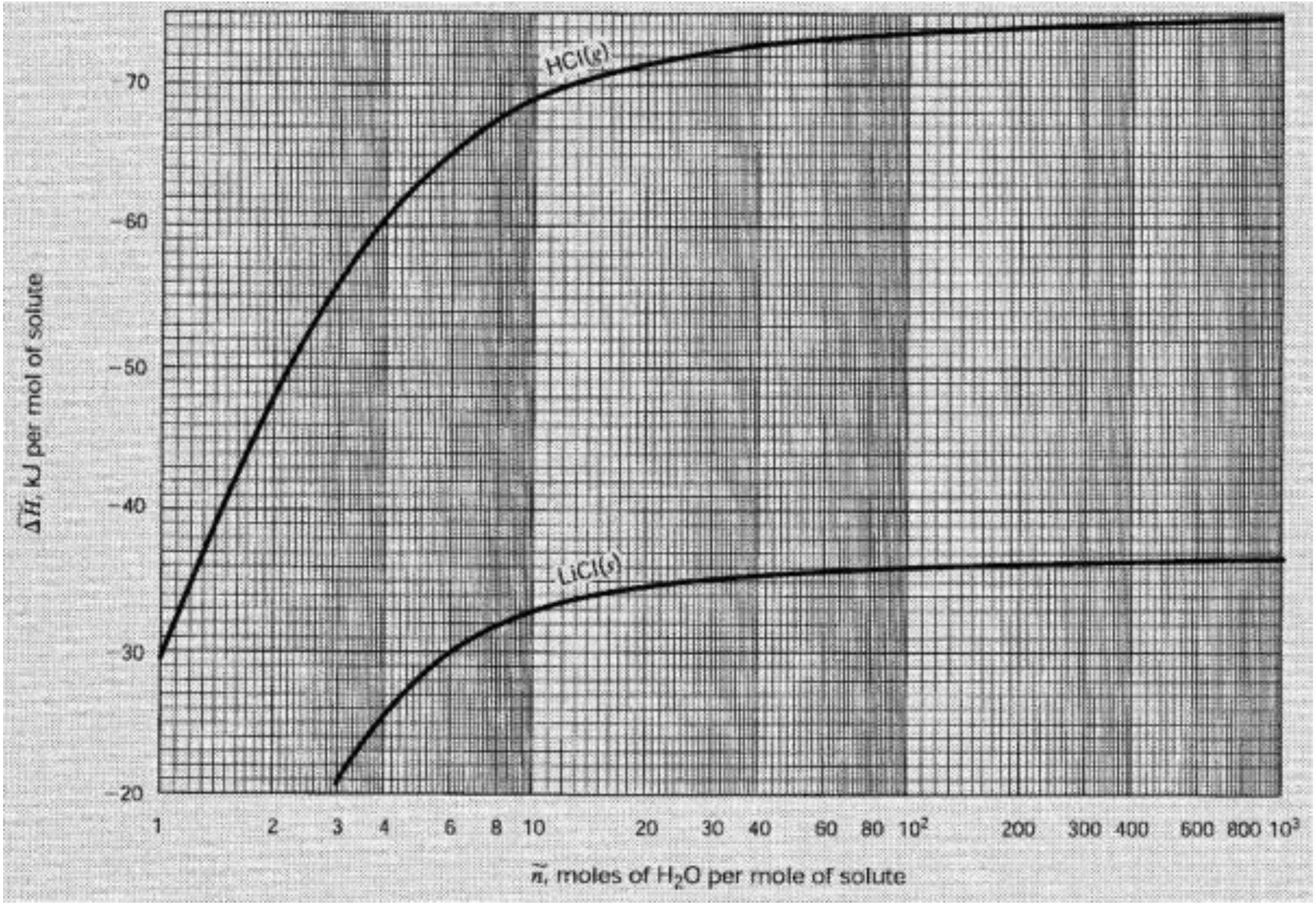
$$\boxed{\Delta\tilde{H} = \frac{\Delta H}{x_1}}$$

In J/mol solution:

In J/mol solute; see for example, your textbook, Felder textbook (Principles 2 course, or Perry's Chemical Engineering Handbook.

Heat of mixing and heat of solution

Fig 12.14



Heat of mixing and heat of solution

Example 12.4. Calculate the heat of formation of LiCl in 12 mol of H_2O at 25°C.

$$\boxed{Li+\frac{1}{2}Cl_2 \rightarrow LiCl_{(s)}}$$

$$\boxed{\Delta H^\circ_{298}=-408610\ J}$$ From Appendix C; Table C.4

$$\boxed{LiCl_{(s)}+12H_2O_{(l)} \rightarrow LiCl(12H_2O)}$$

$$\boxed{\Delta\tilde{H}_{298}=-33614\ J}$$ From **Fig 12.14** at:

$$\tilde{n}=12\,\mathrm{mol\ H_2O}/1\,\mathrm{mol\ LiCl_{(s)}}$$

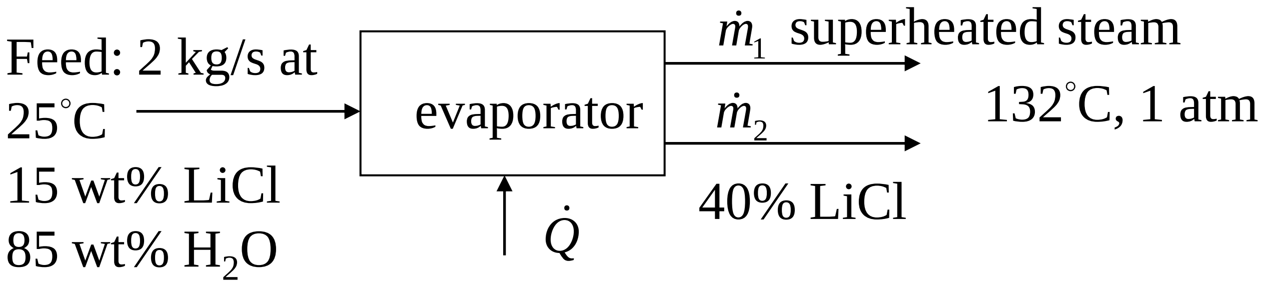
Summation:

$$\boxed{Li+\frac{1}{2}Cl_2+12H_2O_{(l)} \rightarrow LiCl(12H_2O)}$$

$$\boxed{\Delta H^\circ_{298}=-442224\ J}$$

Heat of mixing and heat of solution

Example 12.5. A single-effect evaporator operating at atmospheric pressure concentrates a 15% (by weight) LiCl solution to 40%. The feed enters the evaporator at the rate of 2 kg/s at 25°C. The normal boiling point of a 40% LiCl solution is about 132°C, and its specific heat is estimated as 2.72 kJ/kg °C. What is the heat transfer rate in the evaporator?



LiCl mass balance : $\boxed{(2)(0.15) = (0.4)\dot{m}_2} \longrightarrow \boxed{\dot{m}_2 = 0.75\,\text{kg/s}}$

Total mass balance : $\boxed{(2) = 0.75 + \dot{m}_1} \longrightarrow \boxed{\dot{m}_1 = 1.25\,\text{kg/s}}$

The energy balance: $\boxed{\Delta\dot{H}^t = \dot{Q}}$

Calculation path

Example 12.5

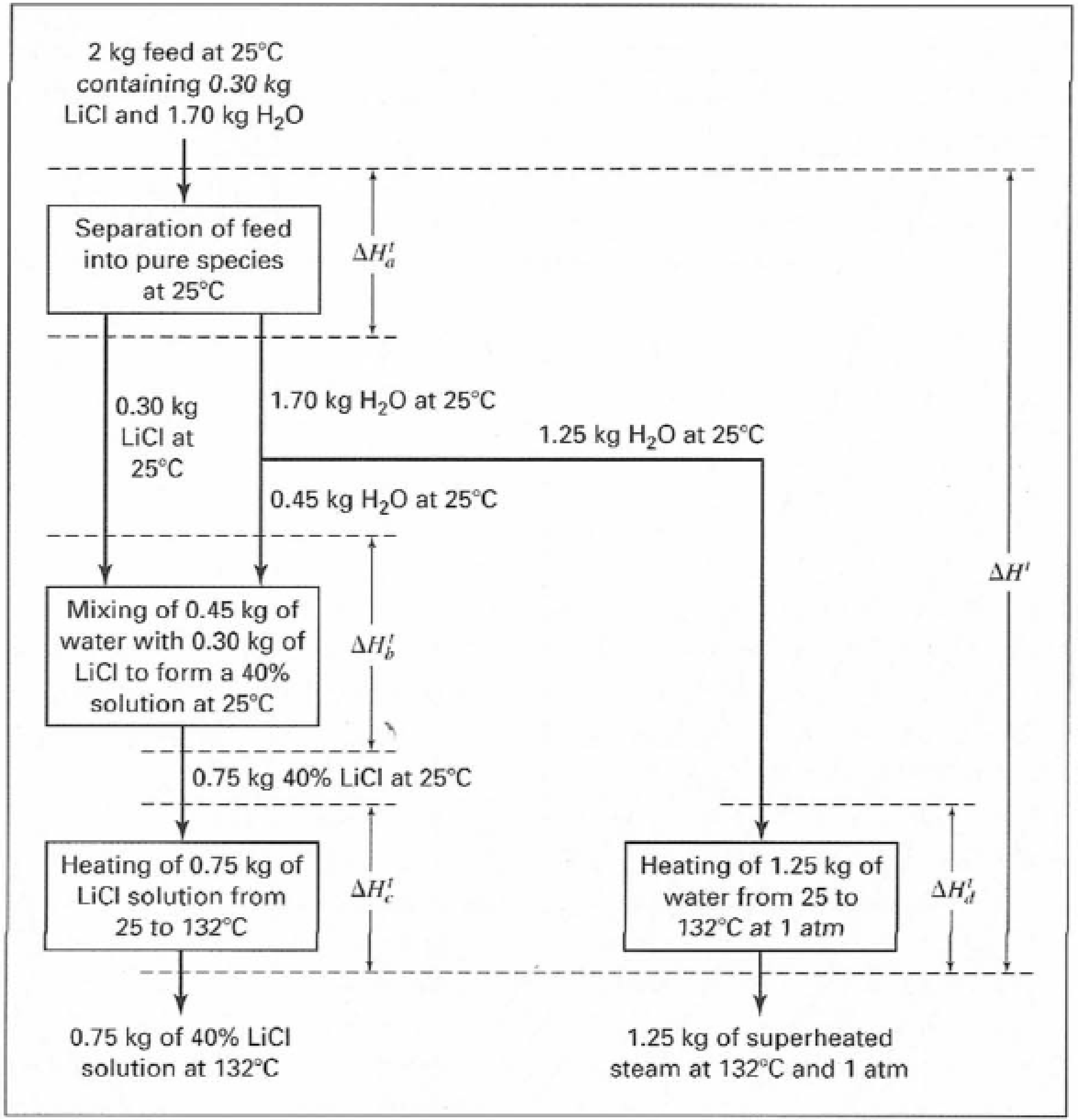


Figure 12.16: Calculational path for process of Example 12.5.

Heat effects of mixing processes

The total enthalpy of the product streams minus the total enthalpy of the feed stream

$$\boxed{\Delta\dot{H}^t = -\Delta\dot{H}_a^t + \Delta\dot{H}_b^t + \Delta\dot{H}_c^t + \Delta\dot{H}_d^t}$$

liquid water is vaporized and heated to 132°C

0.75 kg of 40% LiCl solution is heated to 132°C

mixing of 0.45 kg of water with 0.30 kg of $\text{LiCl}_{(s)}$ to form a 40% solution at 25°C

separation of 2 kg of a 15% LiCl solution into its pure constituents at 25°C; negative because this is unmixing step

- $\Delta\dot{H}_a^t$:

$$\boxed{\frac{(0.3)(1000)}{42.39} = 7.077\,\text{mol LiCl/s}} \qquad \boxed{\frac{(1.7)(1000)}{18.015} = 94.366\,\text{mol H}_2\text{O/s}}$$

From **Fig 12.14** at $\tilde{n} = 94.366\,\text{mol H}_2\text{O}/7.077\,\text{mol LiCl}_{(s)} = 13.33$:

$$\boxed{\Delta\tilde{H} = -33800\ \text{J/mol LiCl}} \longrightarrow \boxed{\Delta\dot{H}_a^t = (-33800)(7.077) = -239250\,\text{J/s}}$$

Heat effects of mixing processes

- ΔH_b^t :

$$\boxed{\frac{(0.3)(1000)}{42.39} = 7.077\,\text{mol LiCl/s}} \qquad \boxed{\frac{(0.45)(1000)}{18.015} = 24.979\,\text{mol H}_2\text{O/s}}$$

From **Fig 12.14** at $\tilde{n} = 24.979\,\text{mol H}_2\text{O}\big/7.077\,\text{mol LiCl}_{(s)} = 3.53$:

$$\boxed{\Delta\tilde{H} = -23260\ \text{J/mol LiCl}} \longrightarrow \boxed{\Delta\dot{H}_b^t = (-23260)(7.077) = -164630\,\text{J/s}}$$

- $\Delta\dot{H}_c^t = \dot{m}Cp\Delta T = (0.75)(2720)(132-25) = 218280\,\text{J}$

$$\boxed{\Delta\dot{H}_c^t = 218280\,\text{J/s}}$$

- $\Delta\dot{H}_d^t = \dot{m}\left[\int_{298.1K}^{373.15} Cp_l\,dT + H^{lv}\Big|_{100^oC} + \left(H^v\Big|_{132^oC,1atm} - H^v\Big|_{100^oC,1atm}\right)\right]$

From Appendix C, Table C. 3: $\dfrac{Cp_l}{R} = 8.712 + 1.25\times10^{-3}T - 0.18\times10^{-6}T^2$

$$\int_{298.1K}^{373.15} \frac{Cp_l}{R}\,dT = 683.3\,K \rightarrow \int_{298.1K}^{373.15} Cp_l\,dT = 5681\,\frac{\text{J}}{\text{mol}}\,\frac{1\,\text{mol}}{0.018015\,\text{kg}} = 315.3\,\text{kJ/kg}$$

Heat effects of mixing processes

From steam tables: $\boxed{H^{lv}\big|_{100^oC} = 2256.9\,\text{kJ/kg}}$ $\boxed{H^{v}\big|_{132^oC,1atm} = 2740.3\,\text{kJ/kg}}$

$$\boxed{H^{v}\big|_{100^oC,1atm} = 2676.0\,\text{kJ/kg}}$$

$$\Delta\dot{H}_d^t = 1.25\big[315.3 + 2256.9 + (2740.3 - 2676.0)\big] = 3295.6\,\text{kJ/s}$$

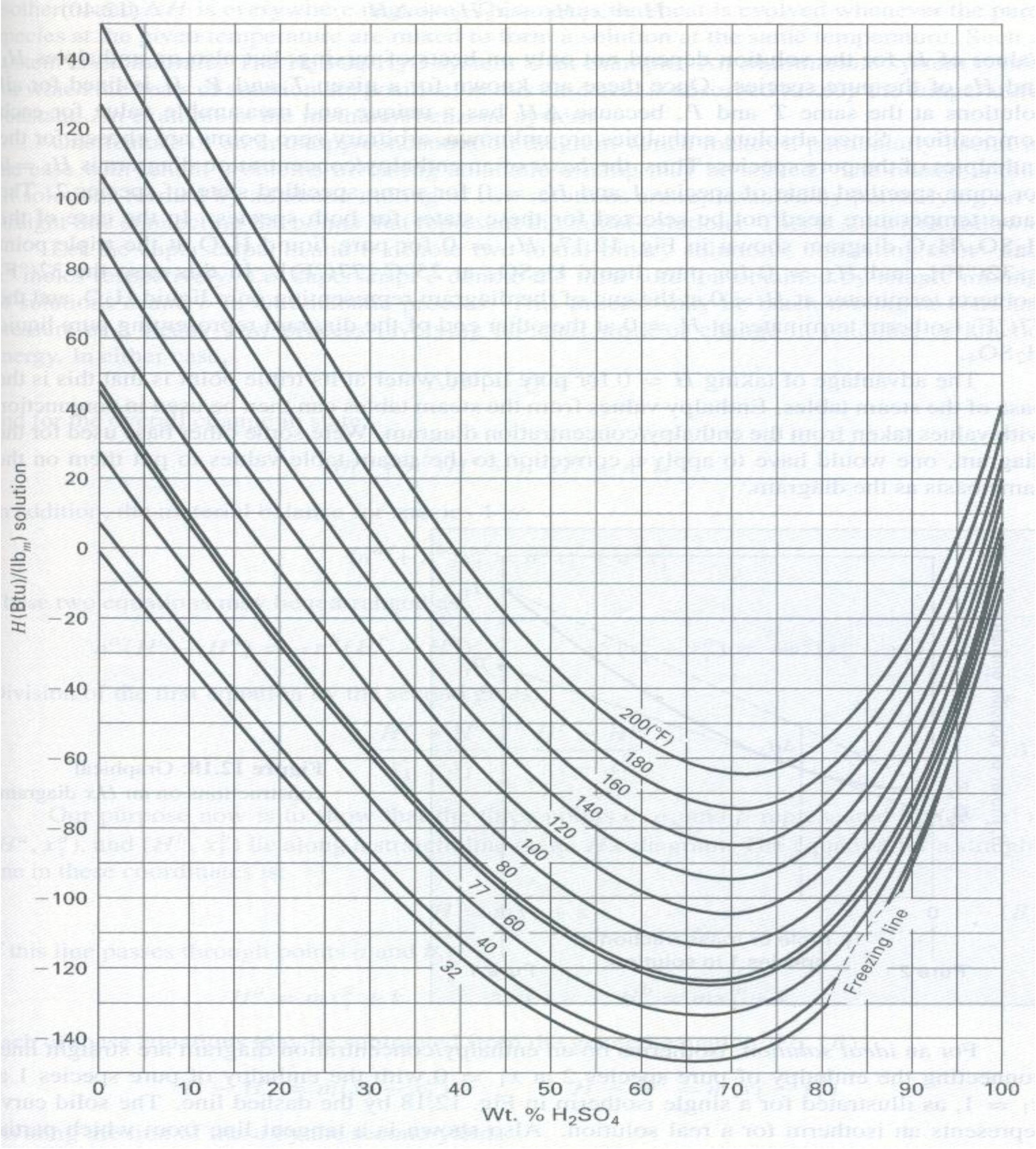
$$\boxed{\Delta H_d^t = 3295600\ \text{J}}$$

$$\boxed{\begin{aligned}\Delta H^t &= -\Delta H_a^t + \Delta H_b^t + \Delta H_c^t + \Delta H_d^t \\ &= -(-239250) + (-164630) + 218280 + 3295600 = 3588500\,J\end{aligned}}$$

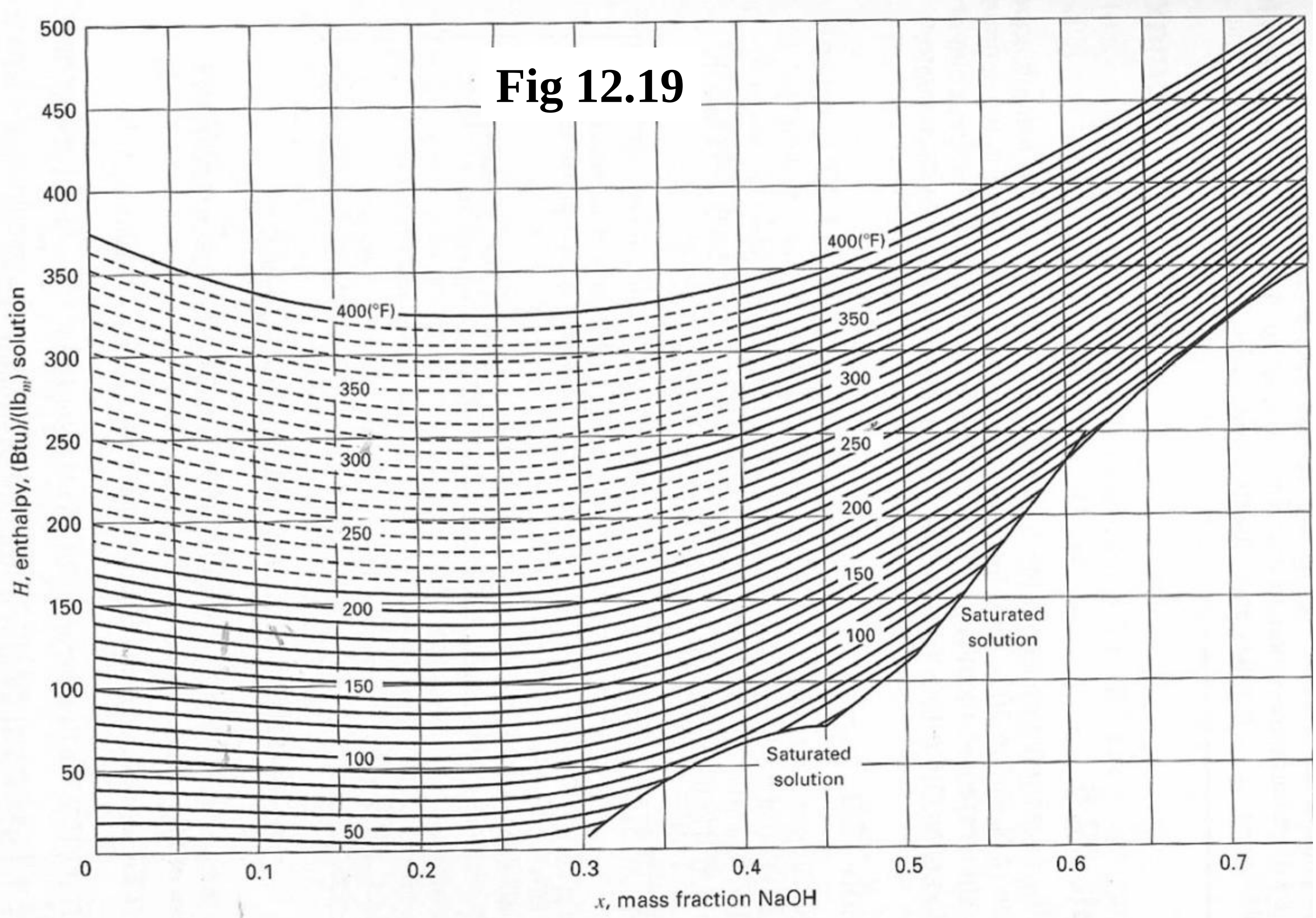
$$\boxed{\dot{Q} = \Delta\dot{H}^t = 3588.5\,\text{kw}}$$

Enthalpy/concentration diagrams

Fig 12.17



Enthalpy/concentration diagrams



Enthalpy/concentration diagrams

Example 12.7. A 10 wt% aqueous NaOH solution at 70°F is mixed with a 70 wt% aqueous NaOH solution at 200°F to form a solution containing 40 wt% NaOH 70°F.

a) If the mixing is done adiabatically, what is the final temperature of the solution?

b) If the final temperature is brought to 70 °F, how much heat must be removed per lbm of solution during this process.

Using **Fig. 12.19**:

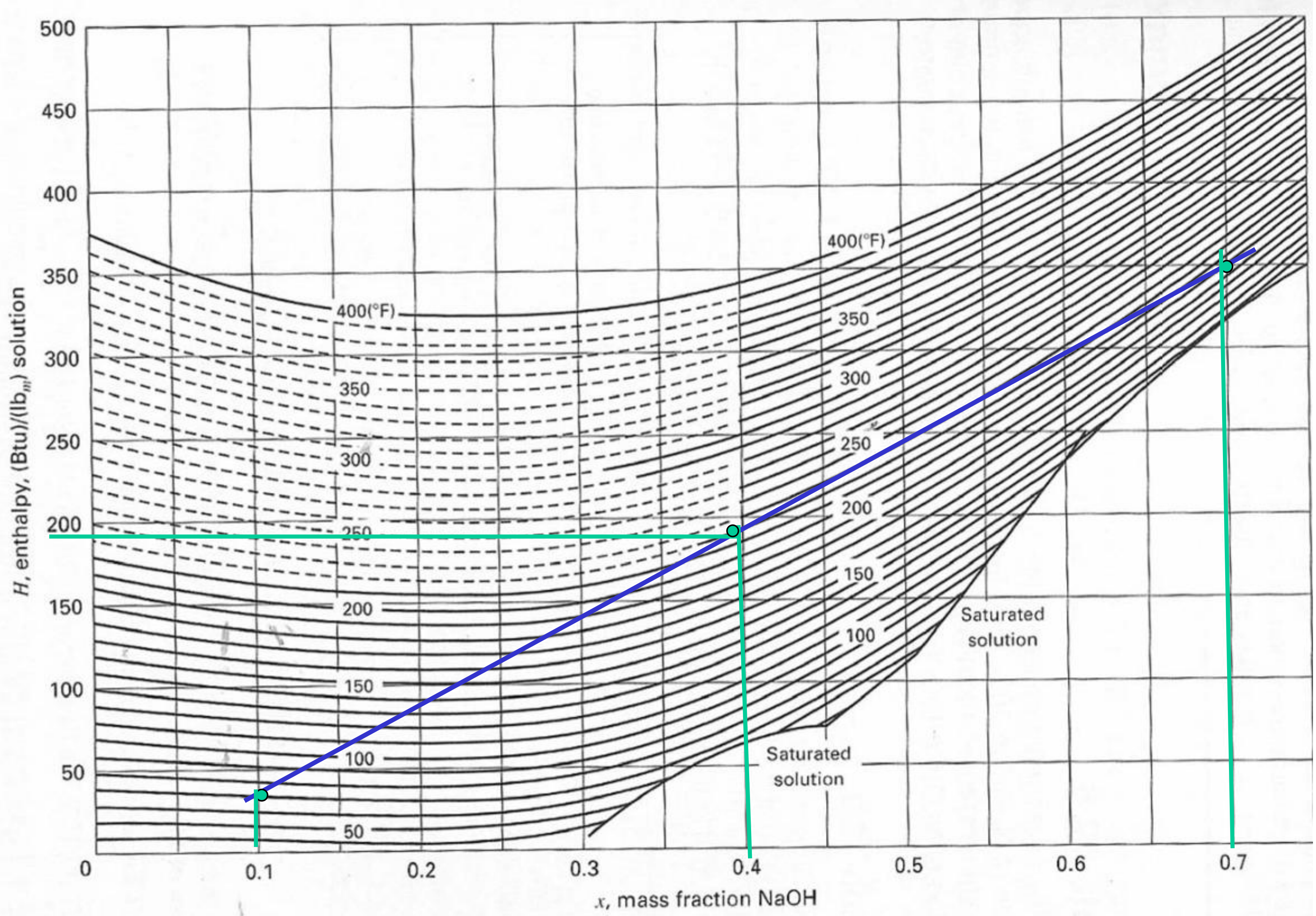
a) Draw straight line on the Hx diagram between the point (x=0.1, T=70 °F) and the point (x=0.7, T=200 °F. The intersection between this line and the vertical line, x = 0.4 give the solution: The intersection occurs at the isotherm **T=220 °F** at which **H=192 Btu/lbm** solution .

b) at x=0.45 and T=70 °F: H=70 Btu/lbm solution.

$$\boxed{Q = \Delta H = (70 - 192) = -122\,\text{Btu/lbm}}$$

Enthalpy/concentration diagrams

Example 12.7



Enthalpy/concentration diagrams

Example 12.9. solid NaOH at 70°F is mixed with H_2O at 70°F to produce a solution containing 45% NaOH at 70°F. How much heat must be transferred per pound mass of solution formed? The enthalpy of pure NaOH at 70°F is 478.7 Btu/lbm

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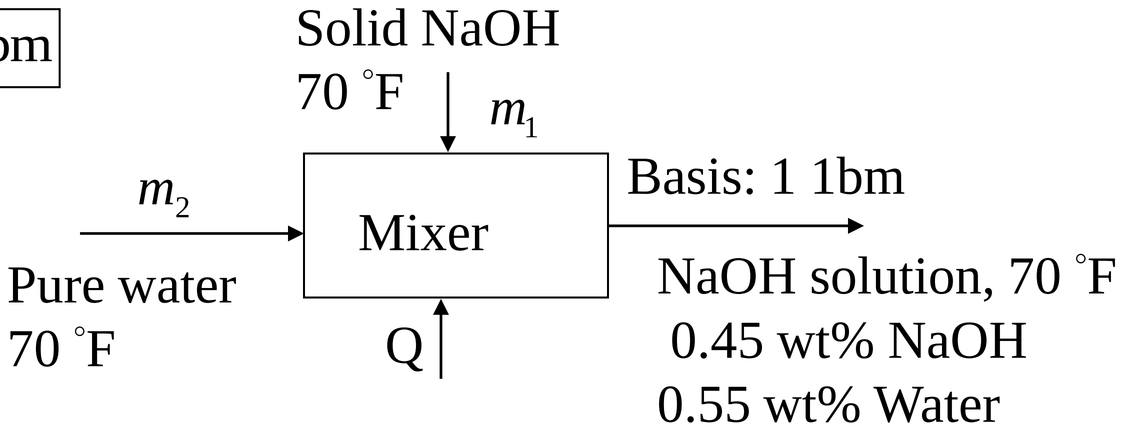
$$\boxed{H_{NaOH} = 478.7 \text{ Btu/lbm}}$$



Solid NaOH
70 °F
m_1

m_2
Pure water
70 °F

Mixer

Q

Basis: 1 1bm

NaOH solution, 70 °F
0.45 wt% NaOH
0.55 wt% Water

NaOH Mass Balance: $m_1 = 0.45 \text{lbm}$

Water Mass Balance: $m_2 = 0.55 \text{lbm}$

Energy balance: $\boxed{Q = \Delta H = (1)(H_{45\% NaOH}) - m_2 H_{water} - m_1 H_{NaOH}}$

Fig 12.19: $\boxed{H_{\mathrm{H_2O}} = 38 \text{ Btu/lbm}}$ $\boxed{H_{45\%\mathrm{NaOH}} = 93 \text{ Btu/lbm}}$

$$\boxed{Q = -143 \text{ Btu/lbm solution}}$$