

# Solution Thermodynamics: Applications

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# Liquid-phase properties from VLE data

- Fugacity

- For species  $i$  in the vapor mixture:  $\hat{f}_i^v = y_i \hat{\phi}_i^v P$

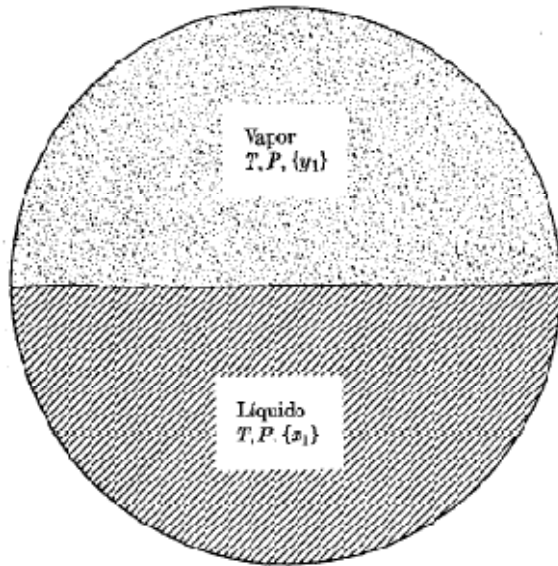
- Vapor/liquid equilibrium:  $\hat{f}_i^v = \hat{f}_i^l$

- The vapor phase is assumed an ideal gas:  $\hat{\phi}_i^v = 1$

- Therefore:  $\hat{f}_i^v = \hat{f}_i^l = y_i P$

- 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.

- Its value increases from zero to  $P_i^{\text{sat}}$  for pure species  $i$



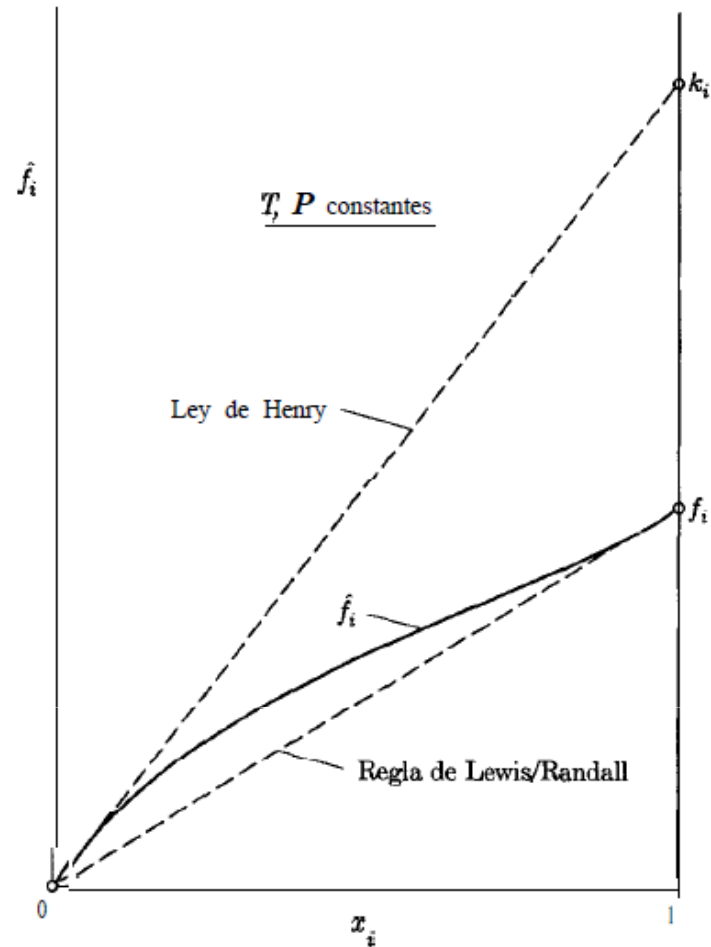
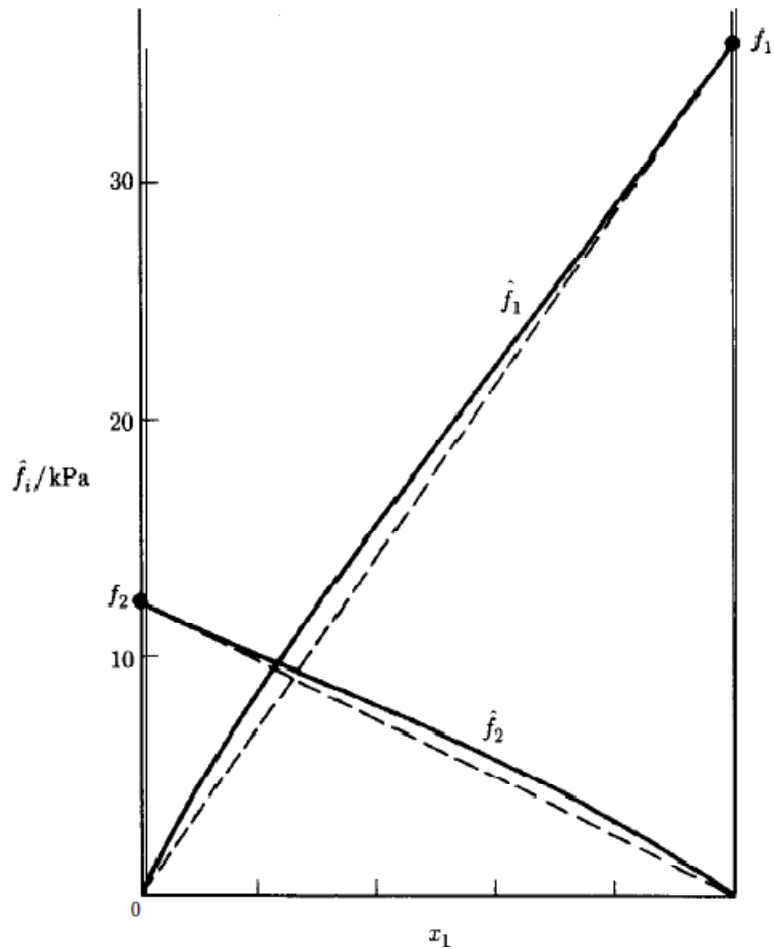
### System MEK(1)/ Toluene(2)

$P/\text{kPa}$	$x_1$	$y_1$	$\hat{f}_1 = y_1 P$	$\hat{f}_2 = y_2 P$	$\gamma_1$	$\gamma_2$
<b>12.30(<math>P_2^{\text{sat}}</math>)</b>	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
<b>36.09(<math>P_1^{\text{sat}}</math>)</b>	1.0000	1.0000	36.090	0.000	1.000	

The first three columns are P- $x_1$ - $y_1$  data.

Columns 4 and 5 are:  $\hat{f}_1 = y_1 P$     $\hat{f}_2 = y_2 P$

Column 6 is:  $\gamma_1 = \frac{\hat{f}_1}{x_1 f_1} = \frac{\hat{f}_1}{\hat{f}_1^{id}} = \frac{y_1 P}{x_1 P_1^{\text{sat}}}$



$$\lim_{x_i \rightarrow 0} \frac{\hat{f}_i}{x_i} = \left( \frac{d\hat{f}_i}{dx_i} \right)_{x_i=0} \equiv H_i$$

Henry's constant, the limiting slope of the  $\hat{f}_i$  vs  $x_i$  curve at  $x_i = 0$ .

Henry's law expresses:  $\hat{f}_i = x_i H_i = y_i P$ , it is approximate valid for small values of  $x_i$

Henry's law

$$x_1 \rightarrow 0$$

Gibbs/Duhem equation

Lewis/Randall rule

$$x_2 \rightarrow 1$$

Gibbs/Duhem equation for binary mixture at const. T and P:

$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0$$

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

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

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

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

Division by  $dx_1$

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

$$dx_1 + dx_2 = 0$$

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

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

The Lewis/Randall rule,

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

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

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

when  $x_1 = 1$ ,

$$\hat{f}_1 = f_1$$

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

limit

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

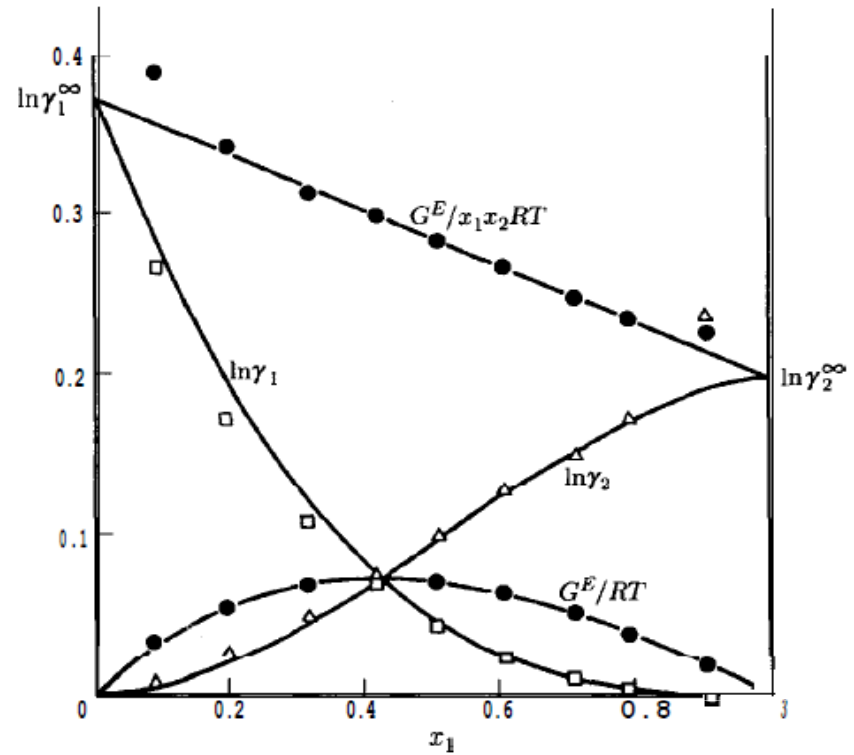
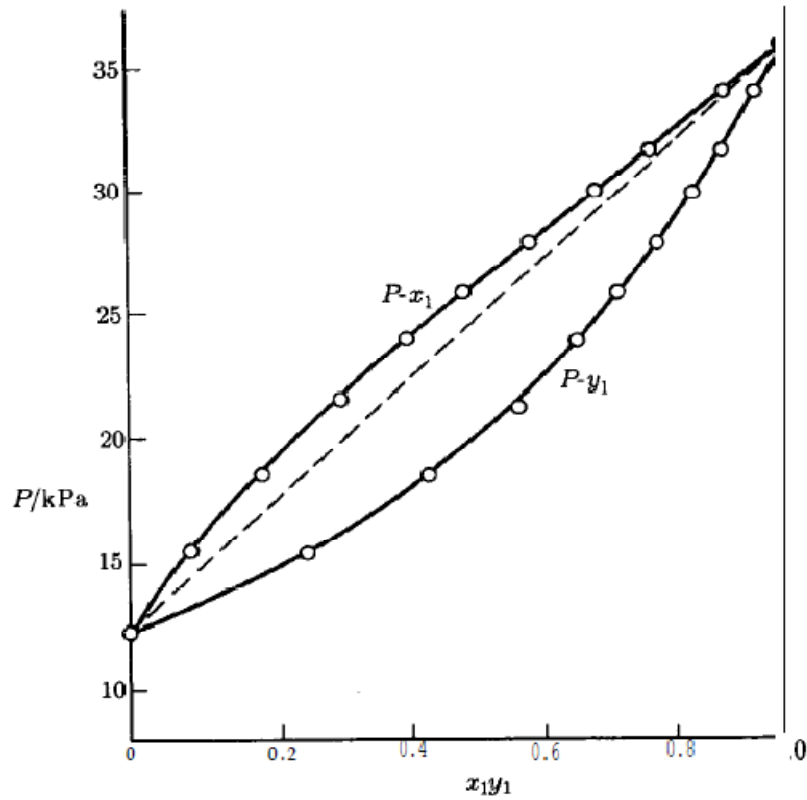
# Excess Gibbs energy

- Table 12.2

– Column 6:

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

$P/\text{kPa}$	$x_1$	$y_1$	$\ln \gamma_1$	$\ln \gamma_2$	$G^E/RT$	$G^E/x_1x_2RT$
12.30( $P_2^{\text{sat}}$ )	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( $P_1^{\text{sat}}$ )	1.0000	1.0000	0.000		0.000	



Positive deviation from Raoult's law behavior:

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

The dimensionless excess Gibbs energy:

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

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

$$\boxed{x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = 0 \quad (\text{const. } T, P)}$$

$$\boxed{\lim_{x_1 \rightarrow 0} \frac{G^E}{x_1 x_2 RT} = \ln \gamma_1^\infty}$$

$$\boxed{\lim_{x_1 \rightarrow 1} \frac{G^E}{x_1 x_2 RT} = \ln \gamma_2^\infty}$$

From Fig 12.5(b), linear relation:

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

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

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

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

Similarly,  $\ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2]$

The Margules equations

Limiting conditions:  $\ln \gamma_1^\infty |_{x_1=0} = A_{12}$   $\ln \gamma_2^\infty |_{x_2=0} = A_{21}$   $\frac{G^E}{RT} = (A_{21} x_1 + A_{12} x_2) x_1 x_2$

$$P = y_1 P + y_2 P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$



# Models for the excess Gibbs energy

- $G^E/RT = f(T, P, \text{composition})$ 
  - At constant T:  $\frac{G^E}{RT} = g(x_1, x_2, \dots, x_N)$

weak

Data fitting, convenient,  
but only for binary system

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

The Redlich/Kister expansion

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

$$A + B = A_{21}$$

$$A - B = A_{12}$$

The Margules equation

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

The van Laar equation

# Local composition models

- Can be applied to multi-component systems

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

- The NRTL(Non-Random-Two-Liquid) equation:

$$\frac{G^E}{x_1 x_2 RT} = \frac{G_{21} \tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12} \tau_{12}}{x_2 + x_1 G_{12}}$$

- The UNIQUAC equation and the UNIFAC method:
  - App. H.

# Property changes of mixing

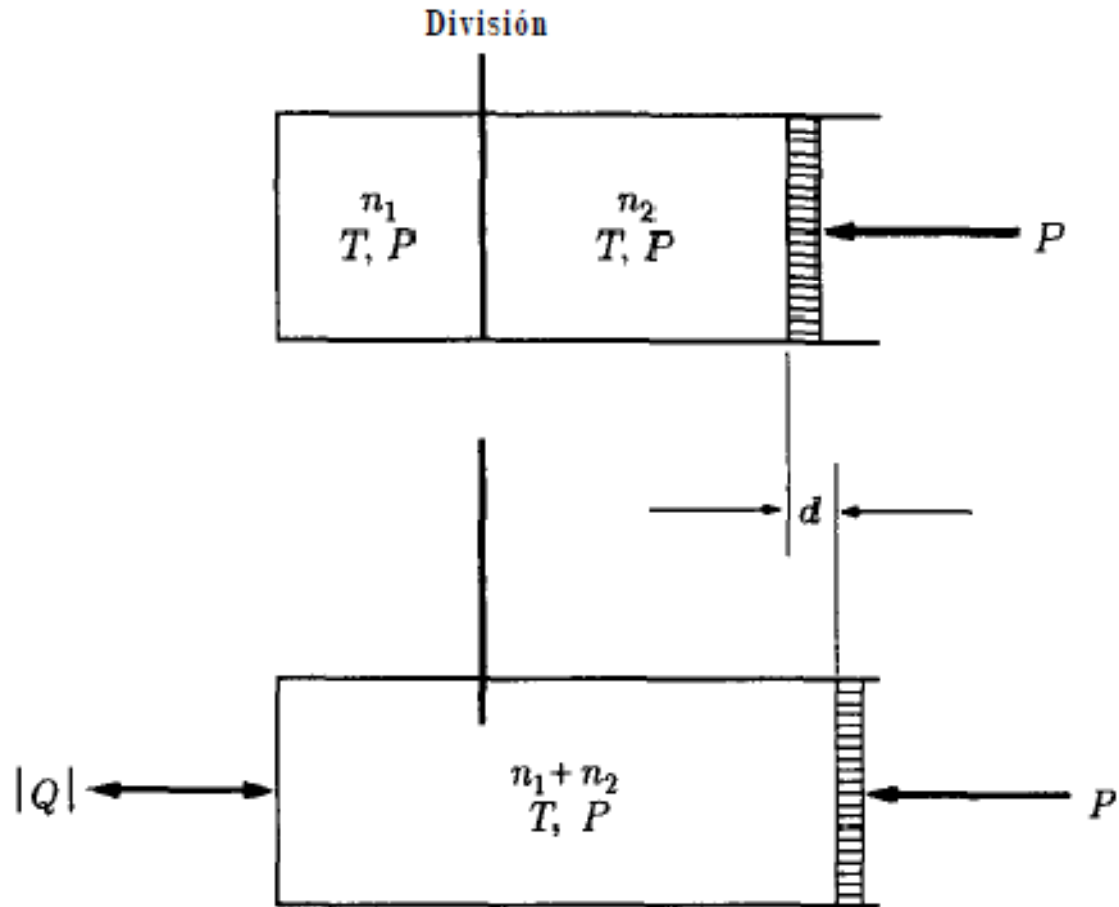
- Excess properties

$$G^E = G - \sum_i x_i G_i - RT \sum_i x_i \ln x_i$$
$$S^E = S - \sum_i x_i S_i + R \sum_i x_i \ln x_i$$
$$V^E = V - \sum_i x_i V_i$$
$$H^E = H - \sum_i x_i H_i$$
$$\Delta M \equiv M - \sum_i x_i M_i$$

The M change of mixing

$$G^E = \Delta G - RT \sum_i x_i \ln x_i$$
$$S^E = \Delta S + R \sum_i x_i \ln x_i$$
$$V^E = \Delta V$$
$$H^E = \Delta H$$

Because of their direct measurability,  $\Delta V$  and  $\Delta H$  are the property changes of mixing of major interest.



$$\Delta V^t = (n_1 + n_2)V - n_1V_1 - n_2V_2$$

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

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

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

The excess enthalpy (heat of mixing) for liquid mixture of species 1 and 2 at fixed T and P is represented by the equation:

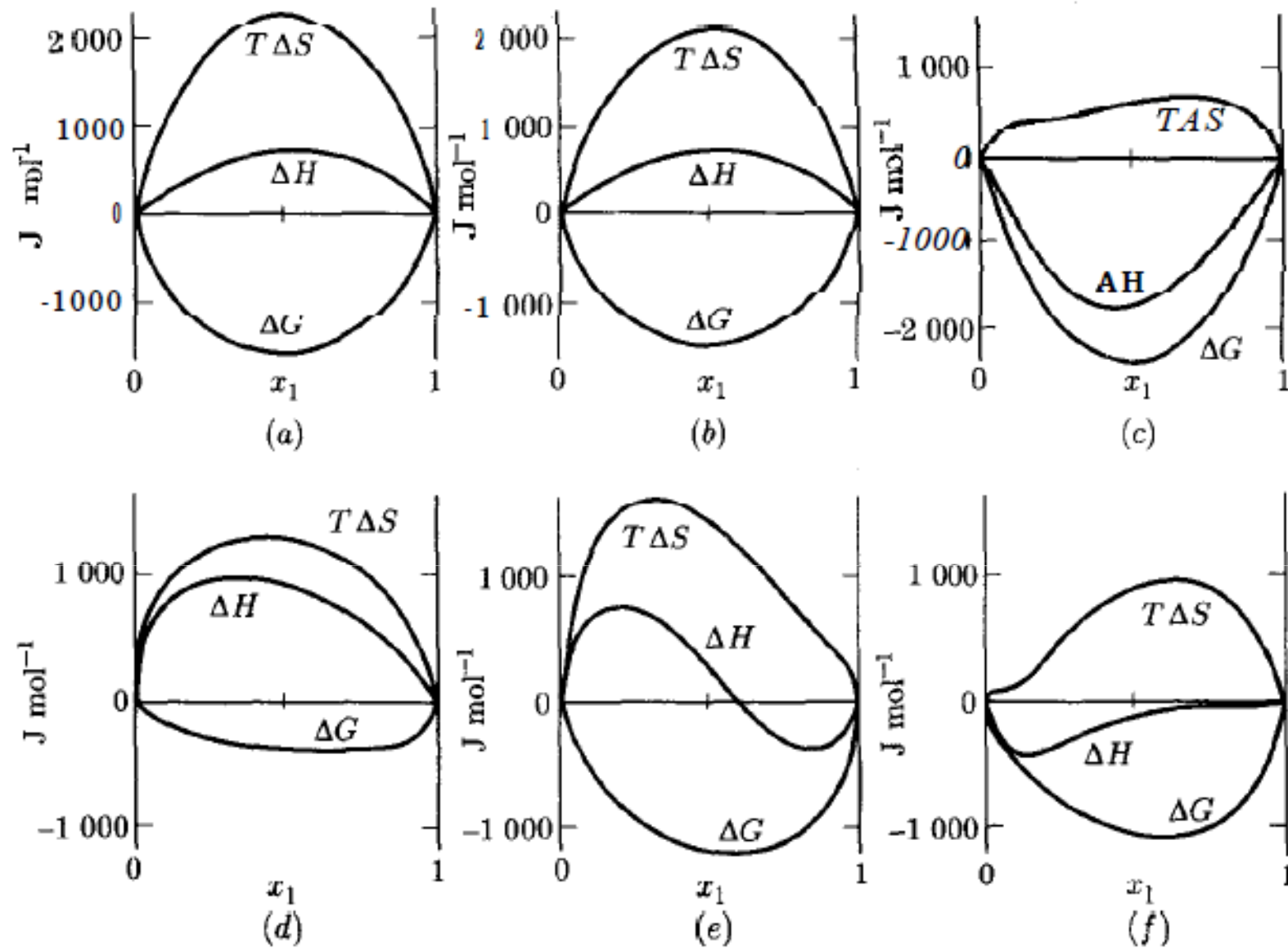
$$H^E = x_1 x_2 (40x_1 + 20x_2)$$

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

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The partial properties:

$\bar{H}_1^E = H^E + (1 - x_1) \frac{dH^E}{dx_1}$	$\bar{H}_2^E = H^E - x_1 \frac{dH^E}{dx_1}$
$H^E = x_1 x_2 (40x_1 + 20x_2)$	
$\bar{H}_1^E = 20 - 60x_1^2 + 40x_1^3$	$\bar{H}_2^E = 40x_1^3$



1. Each  $\Delta M$  is zero for a pure species.
2. The Gibbs energy change of mixing  $\Delta G$  is always negative.
3. The entropy change of mixing  $\Delta S$  is positive.

# Heat effects of mixing processes

- Heat of mixing:  $\Delta H = H - \sum_i x_i H_i$ 
  - For binary systems:  $H = x_1 H_1 + x_2 H_2 + \Delta H$
  - 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:

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