The vapour pressures of each component in a mixture of propanone (acetone, A) and trichloromethane (chloroform, C) were measured at 35 °C with the following results:

x _c	0	0.20	0.40	0.60	0.80	1
$p_{\rm C}/{ m kPa}$	0	4.7	11	18.9	26.7	36.4
p_{A}/kPa	46.3	33.3	23.3	12.3	4.9	0

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants.

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 $p_{\rm C}/{\rm kPa}$ 04.71118.926.736.4 $p_{\rm A}/{\rm kPa}$ 46.333.323.312.34.90

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants.

Raoult's law => straight-line $p_j = x_j p_j^*$ in the region in w

Henry's => straight line $p_1 = x_1 K_1$

in the region in which it is in excess

is tangent to partial vapor pressure curve at low X₁

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Henry's law constants:

 $K_A = 24.5$ kPa for acetone

 $K_c = 23.5$ kPa for chloroform

Focus 5: Simple mixtures

TD description of mixtures

Properties of solutions

Phase diagrams of binary systems

Phase diagrams of ternary systems

Thermodynamic activity

 $\mu_{\rm J} = \mu_{\rm J}^* + RT \ln x_{\rm J}$

Chemical potential [ideal solution]

 $\mu_{\rm J} = \mu_{\rm J}^* + RT \ln x_{\rm J}$

Chemical potential [ideal solution]

 $G_{\rm i} = n_{\rm A} \mu_{\rm A}^{\star} + n_{\rm B} \mu_{\rm B}^{\star}$

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Gibbs energy of mixing [ideal solution]

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Entropy of mixing [ideal solution]

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 $\Delta_{\rm mix}H=0$

Gibbs energy of mixing [ideal solution]

Entropy of mixing [ideal solution]

enthalpy of mixing

$$\mu_{\rm J} = \mu_{\rm J}^* + RT \ln x_{\rm J}$$

Chemical potential [ideal solution]

 $G_{i} = n_{A}\mu_{A}^{*} + n_{B}\mu_{B}^{*}$ $G_{f} = n_{A}(\mu_{A}^{*} + RT\ln x_{A}) + n_{B}(\mu_{B}^{*} + RT\ln x_{B})$ $\Delta_{mix}G = nRT(x_{A}\ln x_{A} + x_{B}\ln x_{B})$ $\Delta_{mix}S = -nR(x_{A}\ln x_{A} + x_{B}\ln x_{B})$

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The change in volume on mixing (ideal), is zero

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 $(\partial G/\partial p)_T = V$

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Chemical potential [ideal solution]

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 $\Delta_{\rm mix}H=0$

The change in volume on mixing (ideal), is zero

 $(\partial G/\partial p)_T = V$ $\Delta_{\min} V = (\partial \Delta_{\min} G/\partial p)_T$

$$\mu_{\rm J} = \mu_{\rm J}^* + RT \ln x_{\rm J}$$

Chemical potential [ideal solution]

 $G_{i} = n_{A} \mu^{*}_{A} + n_{B} \mu^{*}_{B}$ $G_{\rm f} = n_{\rm A}(\mu_{\rm A}^{\star} + RT\ln x_{\rm A}) + n_{\rm B}(\mu_{\rm B}^{\star} + RT\ln x_{\rm B})$ $\Delta_{\rm mix}G = nRT(x_{\rm A}\ln x_{\rm A} + x_{\rm B}\ln x_{\rm B})$ $\Delta_{\rm mix}S = -nR(x_{\rm A}\ln x_{\rm A} + x_{\rm B}\ln x_{\rm B})$ $\Delta_{\min} H = 0$

The change in volume on mixing (ideal), is zero

 $(\partial G/\partial p)_T = V$ $\Delta_{\min} V = (\partial \Delta_{\min} G/\partial p)_T$

 Δ_{mix} G is independent of pressure

Liquid mixtures to form ideal solutions Chemical potential $\mu_{\rm I} = \mu_{\rm I}^* + RT \ln x_{\rm I}$ [ideal solution] $G_{i} = n_{A} \mu^{*}_{A} + n_{B} \mu^{*}_{B}$ $G_{\rm f} = n_{\rm A}(\mu_{\rm A}^{\star} + RT\ln x_{\rm A}) + n_{\rm B}(\mu_{\rm B}^{\star} + RT\ln x_{\rm B})$ $\Delta_{\rm mix}G = nRT(x_{\rm A}\ln x_{\rm A} + x_{\rm B}\ln x_{\rm B})$ $\Delta_{\rm mix}S = -nR(x_{\rm A}\ln x_{\rm A} + x_{\rm B}\ln x_{\rm B})$ $\Delta_{\rm mix}H=0$

The change in volume on mixing (ideal), is zero

 $(\partial G/\partial p)_T = V$ $\Delta_{\min} V = (\partial \Delta_{\min} G/\partial p)_T$

 Δ_{mix} G is independent of pressure

 $\Delta_{\rm mix}V = 0.$

Gibbs energy and entropy of mixing two liquids that form an ideal solution



Gibbs energy and entropy of mixing two liquids that form an ideal solution



Consider a mixture of benzene and methylbenzene, which form an approximately ideal solution, and suppose 1.0 mol $C_6H_6(l)$ is mixed with 2.0 mol $C_6H_5CH_3(l)$.

Find the molar Gibbs energy and entropy of mixing at 25 ^oC

$$\Delta_{\rm mix}G = nRT(x_{\rm A}\ln x_{\rm A} + x_{\rm B}\ln x_{\rm B})$$

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$$\Delta_{\rm mix} G/n = (2.48 \,\rm kJ \, mol^{-1}) \times (0.33 \,\rm ln \, 0.33 + 0.67 \,\rm ln \, 0.67)$$

= -1.6 kJ mol^{-1}

$$\Delta_{\text{mix}} S/n = -(8.3145 \,\text{J K}^{-1} \,\text{mol}^{-1}) \times (0.33 \,\ln 0.33 + 0.67 \,\ln 0.67)$$

= +5.3 $\text{J K}^{-1} \,\text{mol}^{-1}$

 $\Delta_{\min}G = nRT(x_A \ln x_A + x_B \ln x_B) \qquad \Delta_{\min}S = -nR(x_A \ln x_A + x_B \ln x_B)$

A-A, A-B, and B-B interactions are all different.

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A-A, A-B, and B-B interactions are all different.

If $\Delta G > 0$ liquids are immiscible.

If partially miscible => miscible only over a certain range of compositions



$$X^{\mathrm{E}} = \Delta_{\mathrm{mix}} X - \Delta_{\mathrm{mix}} X^{\mathrm{ideal}}$$

Excess function [definition]

$$X^{\rm E} \!=\! \Delta_{\rm mix} X \!-\! \Delta_{\rm mix} X^{\rm ideal}$$



$$V^{E} = \Delta_{mix} V$$

 $H^{E} = \Delta_{mix}H$





benzene/cyclohexane;



(a) $x(C_6H_5)$

Nearly symmetric



Nearly symmetric

 $H^{\rm E} \neq 0$ but $S^{\rm E} = 0$.

A theoretical concept in thermodynamics

 $H^{E} \neq 0$ but $S^{E} = 0$. A theoretical concept in thermodynamics

Entropy change is similar to an ideal solution, but not the enthalpy change

 $H^{\rm E} \neq 0$ but $\dot{S}^{\rm E} = 0$.

$$H^{\rm E} = n\xi RTx_{\rm A}x_{\rm B}$$

$$H^{\rm E} \neq 0$$
 but $S^{\rm E} = 0$.

A measure of A-B interactions compared to A-A and B-B

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A measure of A-B interactions compared to A-A and B-B



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A measure of A-B interactions compared to A-A and B-B





$S^{E} = 0$ ideal value

$S^{E} = 0$ ideal value



 $\Delta_{\min}H$ - T

$S^{E} = 0$ ideal value

 $\Delta_{\rm mix}$ S



$S^{E} = 0$ ideal value

$$\Delta_{\rm mix}G = n\xi RTx_{\rm A}x_{\rm B}$$

 $\Delta_{\rm mix}$ S

$$S^{\rm E} = 0$$

ideal value

$$\Delta_{\text{mix}} G = \overbrace{n\xi RTx_A x_B}^{\Delta_{\text{mix}} H} - T \underbrace{\Delta_{\text{mix}} S}_{-n\xi RTx_A x_B} - T [-nR(x_A \ln x_A + x_B \ln x_B)]$$

$$S^{\rm E} = 0$$

ideal value

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$$S^{\rm E}=0$$

ideal value

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