EXAMPLE

Some properties of N_2 are given below:

density (0°C, 1 atm)	1.25 g L^{-1}
normal boiling point	-195.8°C
normal melting point	-210.01°C
vapor density (at boiling point)	4.61 g L^{-1}
liquid density (at boiling point)	804 g L^{-1}
solid density (at melting point)	820 g L^{-1}
vapor pressure of solid (at melting point)	96.4 mm Hg
enthalpy of vaporization (at boiling point)	47.6 cal g^{-1}
enthalpy of fusion (at melting point)	6.1 cal g^{-1}
critical temperature	126.0 K
critical pressure	33.5 atm

At 1 atm there is a transition from crystalline solid II to the more closely packed crystalline solid I (which is stable at lower temperatures) at 35.61 K.

Plot specific points on the phase diagram of N_2. **Label** the numerical coordinates of all such points along the axes. **Calculate** slopes of curves from available data. **Show** all calculations on the next page.

Identify specific points on the **p** vs **T plot:**

(1 atm, 35.61 K) : SOLID I – SOLID II normal transition point
(1 atm, 63 K) : normal melting point
(1 atm, 77.4 K) : normal boiling point
(33.5 atm, 126.0 K) : critical point
(0.127 atm, 63 K) : vapor pressure of solid at melting point (96.4 mm Hg = 0.127 atm)

Calculate slopes: $dp/dT = \Delta S/\Delta V$ Clapeyron equation

SOLID II – LIQUID equilibrium curve:

At normal melting point, 63 K, $\Delta S = \Delta_{fus}H / T_m$

At normal melting point, 63 K the density of liquid should be slightly greater than at 77.4 K,

$\geq$ ~804 g L^{-1}. If we use 804 g L^{-1} we get the slope

$dp/dT = \Delta_{fus}S/(V_{LIQ} - V_{SOLID})$

$$= \frac{6.1 \text{ cal}}{63 \text{ K}} \times \frac{0.08205 \text{ L atm K}^{-1}}{1.987 \text{ cal K}^{-1}} \Big/ \left(\frac{1}{804} - \frac{1}{820}\right) \text{L}$$

$= +160$ atm K^{-1}

LIQUID – VAPOR equilibrium curve:

At normal boiling point 77.4 K, $\Delta S = \Delta_{vap}H / T_b$

$dp/dT = \Delta_{vap}S/(V_{LIQ} – V_{GAS})$

$$= \frac{47.6 \text{ cal}}{77.4 \text{ K}} \times \frac{0.08205 \text{ L atm K}^{-1}}{1.987 \text{ cal K}^{-1}} \Big/ \left(\frac{1}{4.61} - \frac{1}{804}\right) \text{L}$$

$= +0.115$ atm K^{-1}

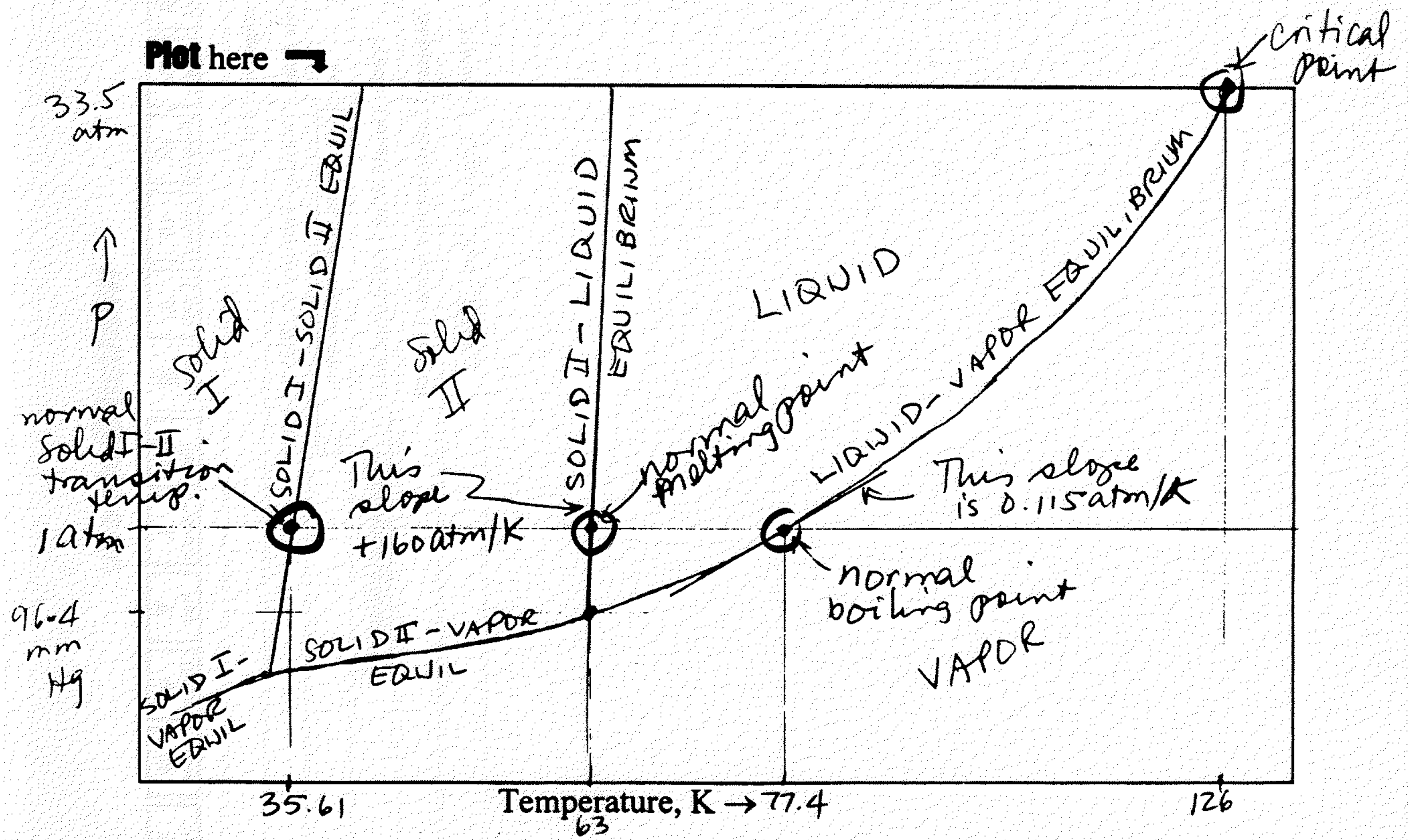
SOLID I – SOLID II equilibrium curve:

$dp/dT = (S_{SOL\ II} – S_{SOL\ I}) / (V_{SOL\ II} – V_{SOL\ I})$

SOLID I is said to be more closely packed: $(V_{SOL\ II} – V_{SOL\ I}) > 0$

SOLID I is said to be more stable at lower T: $(S_{SOL\ II} – S_{SOL\ I}) > 0$

Thus, $dp/dT > 0$



Plot here
critical point
33.5 atm
P
normal Solid I-II transition temp.
1 atm
96.4 mm Hg
Solid I
SOLID I - SOLID II EQUIL
Solid II
This slope +160 atm/K
SOLID II - LIQUID EQUILIBRIUM
normal melting point
LIQUID
LIQUID - VAPOR EQUILIBRIUM
This slope is 0.115 atm/K
normal boiling point
VAPOR
SOLID II - VAPOR EQUIL
SOLID I - VAPOR EQUIL
35.61
Temperature, K → 77.4
63
126

EXAMPLE:

1. At 298 K we have

	$\Delta G_f^{\ominus}{}_{T=298K}$ kcal mol^{-1}	$S^{\ominus}{}_{T=298K}$ cal K^{-1} mol^{-1}
Rhombic sulfur	0	7.62
Monoclinic sulfur	0.023	7.78

Assuming that the entropies vary only slightly with temperature, sketch the value of μ versus T for the two forms of sulfur. From the data, determine the equilibrium temperature for the transformation,

Rhombic sulfur→ Monoclinic sulfur

EXAMPLE:

2. Given the following data for benzene, C_6H_6:

At the normal boiling point, 80.1°C ,
$\Delta_{vap}H$ is 7.353 kcal mol^{-1} , and
C_p for the liquid is 31 cal mol^{-1} K^{-1}
C_p for the vapor is $-0.409 + 77.621\times10^{-3}\,T - 264.29\times10^{-7}\,T^2$ cal mol^{-1} K^{-1}

Assume that benzene vapor behaves ideally. Calculate ΔS for the process:

C_6H_6	→	C_6H_6
(liq, 82.1°C, 1 atm)		(g, 82.1°C, 0.5 atm)

Note that this process occurs at 2° above the normal boiling point.

EXAMPLE:

1. At 298 K we have

	$\Delta G_f^{\ominus}{}_{T=298K}$ kcal mol^{-1}	$S^{\ominus}{}_{T=298K}$ cal K^{-1} mol^{-1}
Rhombic sulfur	0	7.62
Monoclinic sulfur	0.023	7.78

Assuming that the entropies vary only slightly with temperature, sketch the value of μ versus T for the two forms of sulfur. From the data, determine the equilibrium temperature for the transformation,

Rhombic sulfur→ Monoclinic sulfur

$dG = Vdp - SdT$

$d\mu = Vdp - SdT$ [V and S are for 1 mole]

At 1 bar, let S vary only slightly with temperature, integrate between 298 K and T,

$\int d\mu_m = -\int_{298}^{T} S_m dT$ for monoclinic

$\mu_m(T) - \mu_m(298\text{ K}) = -S^{\ominus}_m(T-298)$

$\int d\mu = -\int_{298}^{T} S_r dT$ for rhombic

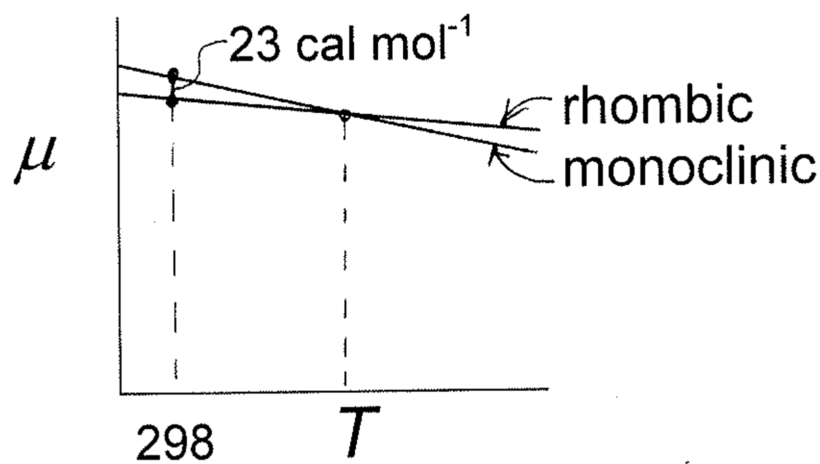
$\mu_r(T) - \mu_r(298\text{ K}) = -S^{\ominus}_r(T-298)$

at equilibrium, $\mu_m(T) = \mu_r(T)$

$\mu_m(298) - S^{\ominus}_m(T-298) = \mu_r(298) - S^{\ominus}_r(T-298)$

$23 \quad -7.78(T-298) = \quad 0.0 \quad -7.62(T-298)$

Solving for T, we find $T = 441.8$ K



EXAMPLE:

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$$C_6H_6 \text{ (liq, 82.1°C, 1 atm)} \rightarrow C_6H_6 \text{ (g, 82.1°C, 0.5 atm)}$$

Note that this process occurs at 2° above the normal boiling point.

(LIQ, 353.3 K, 1 atm) $\rightarrow$(GAS, 353.3 K, 0.5 atm)

$\Delta\boldsymbol{S}$ = ? This is not a reversible change.

Consider 3 REV steps that add up:

(LIQ, 353.3 K, 1 atm) $\rightarrow$(LIQ, 355.3, 1 atm) (a)

(LIQ, 355.3 K, 1 atm) $\rightarrow$(GAS, 355.3, 1 atm) (b)

<u>(GAS, 355.3, 1 atm)$\rightarrow$(GAS, 353.3, 0.5 atm) (c)</u>

(LIQ, 353.3 K, 1 atm) $\rightarrow$(GAS, 353.3, 0.5 atm)

$\Delta\boldsymbol{S} = \Delta\boldsymbol{S}_a + \Delta\boldsymbol{S}_b + \Delta\boldsymbol{S}_c$

$\mathrm{d}\boldsymbol{S} = (\partial\boldsymbol{S}/\partial T)_p\mathrm{d}T + (\partial\boldsymbol{S}/\partial p)_T\mathrm{d}p$

$\mathrm{d}\boldsymbol{S} = (C_p/T)\mathrm{d}T - (\partial V/\partial T)_p\mathrm{d}p$ *using cross derivatives*

$\mathrm{d}\boldsymbol{S} = \delta q_{REV}/T$

now we are ready

$\Delta\boldsymbol{S}_a = \int_{353.3}^{355.3}(C_p^{LIQ}/T)\mathrm{d}T$ since $\mathrm{d}p = 0$

$\Delta\boldsymbol{S}_b = q_{p\ REV}/T = \Delta\boldsymbol{H}_{vap}/355.3$ since $q_p = \Delta\boldsymbol{H}$

$\Delta\boldsymbol{S}_c = \int_{355.3}^{353.3}(C_p^{VAP}/T)\mathrm{d}T - \int_1^{0.5}(\partial V/\partial T)_p\mathrm{d}p$

$\Delta\boldsymbol{S}_a = \int_{353.3}^{355.3}31(\mathrm{d}T/T) = 31\ \ln(355.3/353.3)$

$\Delta\boldsymbol{S}_b = 7.353\times10^3/355.3$

$\Delta\boldsymbol{S}_c =$

$\int_{355.3}^{353.3}(-0.409+77.62\times10^{-3}T-264.29\times10^{-7}T^2/T)\mathrm{d}T$

$- \int_1^{0.5} R\mathrm{d}p/p$ since $(\partial V/\partial T)_p = R/p$ for ideal gas

$\Delta\boldsymbol{S}_c = -0.409(353.3/355.3)$

$+77.62\times10^{-3}(353.3-355.3)$

$-264.29\times10^{-7}(353.3^2-355.3^2)/2 - 1.987\ln(1/0.5)$

$\Delta\boldsymbol{S} = -0.1773 + 20.812 + 1.5138 = 22.15$

Consider the following systems. In each one calculate the pressure p which must be applied in order that equilibrium be established between A and B at the given temperature.

A	B
rhombic sulfur	monoclinic sulfur
p atm	p atm
$\Delta_f G^{\ominus} = 0$	$\Delta_f G^{\ominus} = 0.023$ kcal mol^{-1}
densities:	
1.5 g cm^{-3}	1.2 g cm^{-3}

A		B
H_2 1 atm	Pd membrane allows only H_2 to pass	$H_2 + N_2$ mixture is $4N_2 : 1H_2$ p atm

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densities:	
1.5 g cm^{-3}	1.2 g cm^{-3}

$$\mu^{A} = \mu^{B}$$

$$\mu^{rhom}_{(1atm)} + V_{rhom}\,dp = \mu^{mono}_{(1atm)} + V_{mono}\,dp$$

$$0 + \int_{1atm}^{P} \frac{32}{1.5\times10^{3}}\,dp = 0.023 + \int_{1atm}^{P} \frac{32}{1.2\times10^{3}}\,dp$$

rearrange

$$0.023\times10^{3}\ \text{cal mol}^{-1} = \left(\frac{32}{1.5\times10^{3}} - \frac{32}{1.2\times10^{3}}\right)(P-1)\times\frac{1.987}{.08205}$$

Solve for P

Consider the following systems. In each one calculate the pressure p which must be applied in order that equilibrium be established between A and B at the given temperature.

A		B
H_2 1 atm $P_{H_2} =$ ~~p~~atm	Pd membrane allows only H_2 to pass	$H_2 + N_2$ mixture is $4N_2 : 1H_2$ p atm $x_{H_2} = 0.20$ $P_{H_2} = 0.20\,p$

$$\mu^{A}_{H_2} = \mu^{B}_{H_2}$$

$$\mu^{\ominus}_{H_2(1atm)} = \mu^{\ominus}_{H_2}(1atm) + RT\ln\frac{0.2P}{1}$$

$$0.2P = 1 \quad , \; P = 5\ atm$$

3. Consider the following system: Pure liquid A has a vapor pressure equal to $p_A°$ at 300 K while pure liquid B has a vapor pressure equal to $p_B°$ at 300 K. The molecules of type A have an electric dipole moment equal to 3.2 debye and are capable of forming 1 hydrogen bond per molecule. On the other hand, B molecules do not have a dipole moment at all. B molecules have a greater electric polarizability than A molecules but are incapable of forming hydrogen bonds. ***Which of the following are likely to be true (select all correct ones) about the vapor pressures, boiling temperatures, and compositions of this system?***

A $p_A° < p_B°$ at 300 K
B $p_A° \approx p_B°$ at 300 K
C $p_A° > p_B°$ at 300 K
D $T_{b,A}° < T_{b,B}°$ at 1 atm
E $T_{b,A}° \approx T_{b,B}°$ at 1 atm
F $T_{b,A}° > T_{b,B}°$ at 1 atm

For a 50-50 mol % solution of A and B:

G $p_{total} < ½(p_A° + p_B°)$ at 300 K
H $p_{total} = ½(p_A° + p_B°)$ at 300 K
I $p_{total} > ½(p_A° + p_B°)$ at 300 K
J $p_A < p_A°$ at 300 K
K $p_A > ½p_A°$ at 300 K
L the vapor pressure of A exceeds that given by Raoult's law
M the vapor pressure is depressed compared to that predicted by Raoult's law
N $T_b > T_{b,B}°$ at 1 atm
O $T_b > T_{b,A}°$ at 1 atm
P $T_b < ½(T_{b,A}° + T_{b,B}°)$ at 1 atm
Q $T_b = ½(T_{b,A}° + T_{b,B}°)$ at 1 atm
R $T_b > ½(T_{b,A}° + T_{b,B}°)$ at 1 atm
S mole fraction of A in the vapor < ½
T mole fraction of A in the vapor = ½
U mole fraction of A in the vapor > ½
V mole fraction of A in the vapor $< p_A/(p_A + p_B)$
W mole fraction of A in the vapor $= p_A/(p_A + p_B)$
X mole fraction of A in the vapor $> p_A/(p_A + p_B)$
Y mole fraction of A in the vapor $< p_A°/(p_A° + p_B°)$
Z mole fraction of A in the vapor $= p_A°/(p_A° + p_B°)$
Σ mole fraction of A in the vapor $> p_A°/(p_A° + p_B°)$
Φ fractional distillation leads to pure A in the pot and pure B coming off the distillation column
Δ fractional distillation leads to pure B in the pot and pure A coming off the distillation column
Ω fractional distillation leaves a constant-boiling mixture of A and B in the pot

Circle the letters corresponding to all the correct answers in the boxes below:

A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
P	Q	R	S	T	U	V	W	X	Y	Z	Σ	Φ	Δ	Ω

A ✓$p_A° < p_B°$ at 300 K
B $p_A° \approx p_B°$ at 300 K
C $p_A° > p_B°$ at 300 K
D $T_{b,A}° < T_{b,B}°$ at 1 atm
E $T_{b,A}° \approx T_{b,B}°$ at 1 atm
F ✓ $T_{b,A}° > T_{b,B}°$ at 1 atm

For a 50-50 mol % solution of A and B:

G $p_{total} < ½(p_A° + p_B°)$ at 300 K
H $p_{total} = ½(p_A° + p_B°)$ at 300 K
I ✓ $p_{total} > ½(p_A° + p_B°)$ at 300 K
J ✓$p_A < p_A°$ at 300 K
K ✓ $p_A > ½p_A°$ at 300 K
L ✓ the vapor pressure of A exceeds that given by Raoult's law
M the vapor pressure is depressed compared to that predicted by Raoult's law
N $T_b > T_{b,B}°$ at 1 atm
O $T_b > T_{b,A}°$ at 1 atm
P ✓ $T_b < ½(T_{b,A}° + T_{b,B}°)$ at 1 atm
Q $T_b = ½(T_{b,A}° + T_{b,B}°)$ at 1 atm
R $T_b > ½(T_{b,A}° + T_{b,B}°)$ at 1 atm
S ✓ mole fraction of A in the vapor < ½
T mole fraction of A in the vapor = ½
U mole fraction of A in the vapor > ½
V mole fraction of A in the vapor < $p_A /(p_A + p_B)$
W ✓ mole fraction of A in the vapor = $p_A /(p_A + p_B)$
X mole fraction of A in the vapor > $p_A /(p_A + p_B)$
Y mole fraction of A in the vapor < $p_A° /(p_A° + p_B°)$
Z mole fraction of A in the vapor = $p_A° /(p_A° + p_B°)$
Σ ✓mole fraction of A in the vapor > $p_A° /(p_A° + p_B°)$
Φ fractional distillation leads to pure A in the pot and pure B coming off the distillation column
Δ fractional distillation leads to pure B in the pot and pure A coming off the distillation column
Ω fractional distillation leaves constant-boiling mixture of A and B in the pot

Circle the letters corresponding to all the correct answers in the boxes below:

(A)	B	C	D	E	**(F)**	G	H	**(I)**	**(J)**	**(K)**	**(L)**	M	N	O
(P)	Q	R	**(S)**	T	U	V	**(W)**	X	Y	Z	(Σ)	Φ	Δ	Ω

Problem 3 Explanation of the logic behind the correct choices

Given: The molecules of type A have an electric dipole moment equal to 3.2 debye and are capable of forming 1 hydrogen bond per molecule. On the other hand, B molecules do not have a dipole moment at all. B molecules have a greater electric polarizability than A molecules but are incapable of forming hydrogen bonds.

Based on these properties of the molecules we find that: A-A intermolecular interactions (hydrogen bonding plus dipole-dipole) are stronger than B-B interactions (induced dipole-induced dipole, which depends on the electric polarizability). Also A-A interactions are stronger than A-B interactions (B is incapable of forming hydrogen bonds with other molecules). Since the B molecules have larger electric polarizability, the A-B interactions are very likely also weaker than the B-B interactions. So we have intermolecular interactions A-A > B-B and A-A > A-B to work with, {and likely also B-B > A-B}. All the choices depend on this.

It is the intermolecular interactions that determine the escaping tendency of molecules from the liquid into the vapor. Therefore, A-A > B-B leads to ✓ $p_A° < p_B°$ (A) at the same temperature, which means that A has to be raised to a higher temperature (than B) in order to achieve 1 atm vapor pressure, so its normal boiling temperatures is higher:
✓ $T_{b,A}° > T_{b,B}°$ (F)

In a 50-50 mol% liquid solution of A and B, ✓ $p_A < p_A°$ (J) since only half of the surface molecules are A molecules. If the intermolecular interactions are all comparable (ideal solution), $p_A = ½p_A°$, but the ability of A to escape from a surface in which some of its neighbors are B is greater than in pure liquid A since the strength of intermolecular interactions is A-A > A-B. Thus, ✓ the vapor pressure of A exceeds that given by Raoult's law (L) or ✓ $p_A > ½p_A°$ (K) . Therefore, even if you were not sure whether the magnitude of the interactions is B-B > A-B or B-B ≈ A-B, you would still end up with ✓ $p_{total} > ½ (p_A° + p_B°)$ (I), that is, greater than given by Raoult's law (positive deviations from Raoult's law). The ✓ mole fraction of A in the vapor = $p_A /(p_A+ p_B)$ (W), of course, because this is just Dalton's law of partial pressures: in the gas the pressure contributed by A molecules is proportional to the number of A molecules. If the intermolecular interactions had been all comparable (ideal solution), mole fraction of A in the vapor would have been = $½p_A° /(½p_A°+ ½p_A°)$ which with $p_A° < p_B°$

would have led to ✓mole fraction of A in the vapor < ½ (S) (the vapor has a smaller proportion of the less volatile component.

But since A-A > A-B led to $p_A > ½p_A°$, then the ✓mole fraction of A in the vapor would actually be > $½p_A° /(½p_A°+½p_A°)$ (Σ), i.e., greater than predicted by Raoult's law (positive deviation). Positive deviations from Raoult's law lead to a maximum in the total vapor pressure curve, which in turn leads to a minimum in the boiling point curve for the liquid solution. A minimum in the boiling point curve (a minimum-boiling azeotrope) means that the solution boils at a lower temperature than either pure component or $T_b < ½ (T_{b,A}° + T_{b,B}°)$ (P). Therefore fractional distillation cannot lead to a separation into two pure substances. In this case of a minimum-boiling azeotrope,there are two possibilities depending on whether the azeotropic composition has $x_{A,azeo} > x_A = ½$ or $x_{A,azeo} < ½$. Pretend that here we have $x_{A,azeo} < ½$, then the pot will contain pure A (the higher boiling pure component) and over the top will be vapor that has the composition $x_{A,azeo}$. {If it had been the other way around, $x_{A,azeo} < ½$, then the pot will contain the pure B (which boils at a higher temperature than the azeotrope) while the mixture of azeotropic composition will be collected as vapor over the top of the distillation column.} Unfortunately, I failed to provide either of these two choices in the multiple choice list! I should have included: "✓(Ψ) fractional distillation leads to separation into one pure component and one constant boiling mixture."

1. A solution is formed by mixing 0.3 mol of C_6H_{14} with 0.5 mol of C_7H_{16}. If the solution behaves ideally, and the densities of pure C_6H_{14} and C_7H_{16} are d_6 and d_7 g/mL, respectively, find ΔS, ΔG, ΔH, and ΔV of mixing at 25°C.

EXAMPLE:

The activity of pure liquid water at 1 bar is 1 according to the definition of the standard state as a pure liquid at 1 bar.

Calculate the activity of pure liquid water at 50°C and 10^4 bar, given that the integral for liquid water at 50°C, $\int V_m\, dp$ between 1 bar and 10^4 bar is = 16359 J mol^{-1}.

EXAMPLE: **1.** A solution is formed by mixing 0.3 mol of C_6H_{14} with 0.5 mol of C_7H_{16}. If the solution behaves ideally, and the densities of pure C_6H_{14} and C_7H_{16} are d_6 and d_7 g/mL, respectively, find $\Delta\boldsymbol{S}$, $\Delta\boldsymbol{G}$, $\Delta\boldsymbol{H}$, and $\Delta\boldsymbol{V}$ of mixing at 25°C.

$\Delta\boldsymbol{S}$ of mixing = $-\,n_{tot}\,R\{\,x_A \ln x_A + x_B \ln x_B\,\}$

$= -0.8 \text{ mol} \times 1.98718 \text{ cal mol}^{-1}\text{ K}^{-1}$

$\times\{(0.3/0.8)\ln(0.3/0.8) + (0.5/0.8)\ln(0.5/0.8)\}$

$= +1.05 \text{ cal K}^{-1}$

Since mixing leads to mixture that behaves ideally, and $dT=0$, $\therefore\ \Delta\boldsymbol{H} = 0$

$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$

$d\boldsymbol{G} = d\boldsymbol{H} - \boldsymbol{S}dT - Td\boldsymbol{S}$

At constant T, $dT=0$, $\therefore\ \Delta\boldsymbol{G} = \Delta\boldsymbol{H} - T\Delta\boldsymbol{S}$

$\Delta\boldsymbol{G}$ of mixing at 25°C =

$$0 - n_{tot}\,RT\{\,x_A \ln x_A + x_B \ln x_B\,\}$$

$= -0.8 \text{ mol} \times 298 \text{ K} \times 1.98718 \text{ cal mol}^{-1}\text{ K}^{-1}$

$\times\{(0.3/0.8)\ln(0.3/0.8) + (0.5/0.8)\ln(0.5/0.8)\}$

$= -313.33 \text{ cal}$

$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S} \qquad \boldsymbol{H} \equiv \boldsymbol{U} + pV$

$\therefore \; d\boldsymbol{G} = d\boldsymbol{U} + p dV + V dp - T d\boldsymbol{S} - \boldsymbol{S} dT$

Now let us get rid of some terms above.

First Law says $\quad d\boldsymbol{U} = \eth q + \eth W$

Second law says $\quad T d\boldsymbol{S} = \eth q_{rev}$

For a reversible change,

$\eth W = - p_{op} dV \quad$ turns into $- p dV$

$\therefore \quad d\boldsymbol{U} = T d\boldsymbol{S} - p dV$

substitute into $d\boldsymbol{G}$ to get

$d\boldsymbol{G} = V dp - \boldsymbol{S} dT$

Now we are ready:

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

$(\partial \Delta \boldsymbol{G}/\partial p)_T = \Delta V$

Since there is no p dependence in the expression:

$\Delta \boldsymbol{G}$ of mixing = $- n_{tot} RT\{ x_A \ln x_A + x_B \ln x_B \}$

$\therefore \; \Delta V$ of mixing $= 0$

EXAMPLE:

The activity of pure liquid water at 1 bar is 1 according to the definition of the standard state as a pure liquid at 1 bar.

Calculate the activity of pure liquid water at 50°C and 10^4 bar, given that the integral for liquid water at 50°C,

$\int V_m \, dp$ between 1 bar and 10^4 bar is = 16359 J mol^{-1}.

Question: What is $a_{LIQ}(323\text{ K}, 10^4\text{ bar})$?

Start from $dG = -S dT + V dp$

$d\mu_{LIQ}(T,p) = V_{LIQ}\,dp$ *for a given temperature*

Integrating between p = 1 bar and $p = p_2$

$\mu_{LIQ}(T,p_2) - \mu_{LIQ}(T, 1\text{ bar}) = \int V_m\,dp$ ⊙

Definition of activity:

$\mu_{LIQ}(T,p_2) = \mu_{LIQ}{}^{\ominus}{}_T + RT \ln a_{LIQ}(T,p_2)$

$\mu_{LIQ}(T,p_2) - \mu_{LIQ}(T, 1\text{ bar})$

$= RT \ln\{a_{LIQ}(T,p_2)/ a_{LIQ}(T,1\text{ bar})\}$

$a_{LIQ}(T,1\text{ bar}) = 1$ Definition of $\ominus$

Therefore, from ⊙

$\int V^{LIQ}{}_m\,dp = RT \ln\{ a_{LIQ}(T,p_2)/1\}$

$16359\text{ J mol}^{-1} = RT \ln a_{LIQ}(323\text{ K}, 10^4\text{ bar})$

$\ln a_{LIQ}(323\text{ K}, 10^4\text{ bar})$

$= 16359/(8.3144\times323) = 6.09$

$\therefore a_{LIQ}(323\text{ K}, 10^4\text{ bar}) = 439$ dimensionless

$\int V^{LIQ}_m \, dp = RT \ln a_{\mathrm{LIQ}}(T,p_2)$

ASIDE: Incidentally,

$a_{\mathrm{LIQ}}(T,p_2)$ is also =

$f_{\mathrm{VAP}}(T,p_2)/\, f_{\mathrm{VAP}}(T,1\ \mathrm{bar})$

which reinforces the identification of activity with the chemical potential.

This is how we do it for this system:

Liquid and vapor at equilibrium

$\mu_{\mathrm{LIQ}}(T,1\ \mathrm{bar}) = \mu_{\mathrm{VAP}}(T,1\ \mathrm{bar})$ (2)

$\mu_{\mathrm{LIQ}}(T,p_2) = \mu_{\mathrm{VAP}}(T,p_2)$ (1)

subtract equation (2) from eq (1)

$\mu_{\mathrm{LIQ}}(T,p_2) - \mu_{\mathrm{LIQ}}(T,1\ \mathrm{bar})$

$= \mu_{\mathrm{VAP}}(T,p_2) - \mu_{\mathrm{VAP}}(T,1\ \mathrm{bar})$

But, ***for the gas***,

$\mu_{\mathrm{VAP}}(T,p_2) = \mu_{\mathrm{GAS}}{}^{\ominus}{}_T + RT \ln f(T,p_2)$ (3)

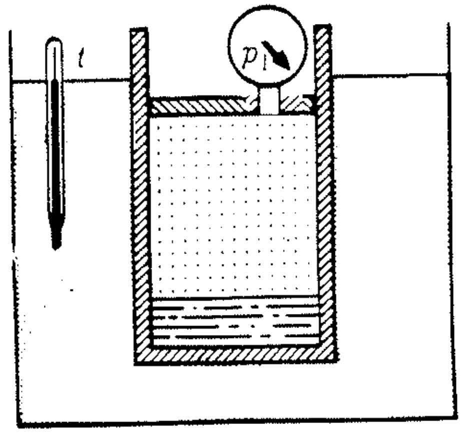
$\mu_{\mathrm{VAP}}(T,1\ \mathrm{bar}) = \mu_{\mathrm{GAS}}{}^{\ominus}{}_T + RT \ln f(T,1\ \mathrm{bar})$ (4)

$\therefore\ \mu_{\mathrm{LIQ}}(T,p_2) - \mu_{\mathrm{LIQ}}(T,1\ \mathrm{bar})$

$= RT \ln\{f_{\mathrm{VAP}}(T,p_2)/\, f_{\mathrm{VAP}}(T,1\ \mathrm{bar})\}$

$\int V^{LIQ}_m \, dp = RT \ln\{f_{\mathrm{VAP}}(T,p_2)/\, f_{\mathrm{VAP}}(T,1\ \mathrm{bar})\}$

2. A mixture of 0.3 moles of liquid A and 0.2 moles of liquid B are placed in the container shown → and the ideal solution is allowed to come to thermal and mechanical equilibrium. The bath temperature is maintained at 21.5°C. The pressure gauge reads 0.060 atm.



At their normal boiling points 110.6°C and 80.1 °C respectively, the enthalpies of vaporization of A and B are respectively, 34.4 and 30.8 kJ mol^{-1} and the densities of liquid A and B at this temperature are respectively 9.407 and 11.247 mol L^{-1}. **Describe the system at equilibrium** by filling in the following table with numbers (not formulas) and their corresponding units.

	numerical value and units
vapor pressure of pure liquid A at 21.5°C	
vapor pressure of pure liquid B at 21.5°C	
molefraction of B in the liquid phase	
partial pressure of A in the vapor	
molefraction of A in the vapor phase	
number of moles of liquid	
number of moles of vapor	
number of moles of A in the liquid phase	
number of moles of B in the vapor phase	

Provide the basis for your numerical answers by doing the derivations and calculations in this space and on the next page:

$d\mu_{LIQ} = d\mu_{VAP}$

$d\mu_{LIQ} = -\boldsymbol{S}_{m,LIQ}\, dT + V_{m,LIQ}\, dp$

$d\mu_{VAP} = -\boldsymbol{S}_{m,VAP}\, dT + V_{m,VAP}\, dp$

$-\boldsymbol{S}_{m,LIQ}\, dT + V_{m,LIQ}\, dp = -\boldsymbol{S}_{m,VAP}\, dT + V_{m,VAP}\, dp$

$(\boldsymbol{S}_{m,VAP} - \boldsymbol{S}_{m,LIQ})dT = (V_{m,VAP} - V_{m,LIQ})dp$

$dp/dT = (\boldsymbol{S}_{m,VAP} - \boldsymbol{S}_{m,LIQ}) / (V_{m,VAP} - V_{m,LIQ})$

the ***Clapeyron equation***

$(\boldsymbol{S}_{m,gas} - \boldsymbol{S}_{m,liquid}) = \Delta_{vap} \boldsymbol{H} / T$

$dp/dT = \Delta_{vap}\boldsymbol{H}/\{T(V_{m,gas} - V_{m,liquid})\}$

On this curve are sets of (p,T) values at which liquid coexists with gas.

Since $V_{m,gas} >> V_{m,liquid}$ and

if $\Delta_{vap}\boldsymbol{H}$ *is only weakly dependent on T,*

and if ideal gas behavior, $V_{m,gas} \approx RT/p$, then

$dp/dT = \Delta_{vap}\boldsymbol{H}p/RT^2$

$\int dp/p \approx \Delta_{vap}\boldsymbol{H}/R \int d(-1/T)$

integrate from the normal boiling point to any other (p, T)

$$\ln (p/1 \text{ atm}) \approx \Delta_{vap}H/R \left[-\frac{1}{T} + \frac{1}{T_b} \right]$$

Definition of normal boiling point:

at the normal boiling point $T = 110.6+273$, liquid A has an equilibrium vapor pressure equal to 1 atm. At some other temperature $T = 21.5+273.1$, the vapor pressure of pure liquid A is given by the Clapeyron eqn:

$$\ln (p/1 \text{ atm}) \approx (34.4\times10^3/8.3144) \left[-\frac{1}{294.6} + \frac{1}{383.7} \right]$$

Solve for p

$p = p^*_A(T = 294.6) = 0.03834$ atm Answer

Do the same for B, the vapor pressure of pure liquid B is given by:

$\ln (p/1\text{ atm}) \approx$

$$(30.8\times10^3/8.3144)\left[-\frac{1}{294.6}+\frac{1}{353.2}\right]$$

solve for p

$p = p^*_B(T = 294.6) = 0.1245$ atm **Answer**

Given that an ideal solution is formed by A and B, the partial vapor pressures are given by Raoult's law

$p_A/p^*_A = x_A \quad p_B/p^*_B = x_B$

Raoult's law

$p = p_A + p_B = x_A\,p^*_A + x_B\,p^*_B$

summing up the partial pressures

$0.060\text{ atm} = x_A(0.0383) + x_B(0.1245)$

$= (1-x_B)(0.0383) + x_B(0.1245)$

solve for x_B

$x_B = 0.25 \quad \therefore x_A = 0.75$ **Answer**

$p_A = x_A\,p^*_A = 0.75(0.03834\text{ atm})$

$= 0.02875$ atm **Answer**

molefraction of A in the vapor is $y_A = p_A/p$
$= 0.02875/ 0.060 = 0.479$ **Answer**

Conservation of moles of each component gives the *lever rule*:

$n_{LIQ}\,(x_A - X_A) = n_{VAP}\,(X_A - y_A)$

Given: total moles = 0.2+0.3 and molar composition: $X_A = 0.3/(0.2+0.3) = 0.60$ and $x_A = 0.75$ $y_A = 0.479$ from above calculations. Therefore,

$n_{LIQ}(0.75 - 0.60) = n_{VAP}(0.60 - 0.479)$
$= (0.50 - n_{LIQ})(0.60 - 0.479)$

solve for n_{LIQ}

$n_{LIQ} = 0.223$ moles **Answer**

By difference, $n_{VAP} = 0.\ 277$ moles **Answer**

moles of A in the liquid = $x_A\, n_{LIQ}$
$= 0.75(0.223) = 0.167$ moles **Answer**

moles of B in the vapor = $y_B\, n_{VAP}$
$= (1 - 0.479)(0.277) = 0.144$ moles **Answer**

5. In each of the following systems, it is desired that equilibrium be maintained between the two sides $\mathcal{A}$ and $\mathcal{B}$ by adjusting one variable (***bold***). **Calculate the value** that this variable has to be set to in each case, so as to maintain equilibrium.

$\mathcal{A}$	$\mathcal{B}$	Equilibrium condition, answers
fresh water semi membrane $T = 298$ K $p = 0.0313$ atm	sea water permeable brane 35000 ppm of dissolved salts ($MW = 58.5$ g mol^{-1}) by weight $T = 298$ K $\boldsymbol{p = ?}$	❀ μ ( ) = μ ( )
liquid D density 55 mol L^{-1} $T = 298$ K $p = 200$ atm	ideal vapor D + insoluble gas E, $T = 298$ K $p_D + p_E = 200$ atm $\boldsymbol{p_D = ?}$	$p^*_D = 0.60$ atm ❀ μ ( ) = μ ( )
water with dissolved CO_2 (0.1 mole %) $T = 278$ K	CO_2 gas $T = 278$ K $\boldsymbol{p_{CO_2} = ?}$	$K_H = 1.25 \times 10^6$ atm at 278 K ❀ μ ( ) = μ ( )
liquid water density 55.55 mol L^{-1} $\boldsymbol{T = ?}$	water vapor $p = 0.20$ bar T = same	$\Delta_{vap}H = 40.7$ kJ mol^{-1} at 373 K ❀ μ ( ) = μ ( )

❀ $\mu_{H2O,\ solution}(T, p, x_{H2O})$

$$= \mu^*_{H2O,\ liquid}(T,\ 0.0313\ \text{atm}) \quad (1)$$

If the solution is ideal, then

$\mu_{H2O,solution} = \mu^*_{H2O,liquid} + RT \ln x_{H2O}$ (ideal solution)

specifically, 35000 grams of salt per 10^6 grams water means

x_{salts}

$$= (35000/58.5)/\{35000/58.5 + 10^6/18\}$$
$$= 0.01065$$

$x_{H2O} = (1 - x_{salts}) = 0.98935$

$\mu_{H2O,\ solution}(T, p, x_A)$

$$= \mu^*_{H2O,\ liquid}(T, p) + RT \ln x_{H2O} \quad (2)$$

Eq. (2) substituted into (1) gives:

$\mu^*_{H2O,\ liquid}(T,\ p) + RT \ln x_{H2O}$

$$= \mu^*_{H2O,\ liquid}(T,\ 0.0313\ \text{atm})$$

rearrange to:

$\mu^*_{H2O,\ liquid}(T, p) - \mu^*_{H2O,\ liquid}(T,\ 0.0313\ \text{atm})$

$$= -RT \ln x_{H2O}$$

Since $(\partial \mu / \partial p)_T = V_m$, the left hand side is

$$\int_{0.0313}^{p} V_m \, dp = V_m (p - 0.0313)$$

$= V_m (p - 0.0313)$

$\therefore V_m (p - 0.0313) = -RT \ln x_{H2O}$

This is the working eqn.

$V_{m,\,H2O} = (18/1000)$

and $\ln 0.98935 = -0.010707$ solve for p

$(p - 0.0313)$

$= 0.082057 \times 298 \times 0.010707 / (18/1000)$

$= 14.545$ atm

$p = 14.577$ atm Answer

❀ $\mu_{\text{D, LIQ}}(T, 200 \text{ atm}) = \mu_{\text{D, VAP}}(T, p_D)$

❀ $\mu^*_{\text{D, LIQ}}(T, p^*_D) = \mu_{\text{D, VAP}}(T, p^*_D)$

in the absence of gas E

Subtract to get:

$$\mu_{\text{D, LIQ}}(T, 200 \text{ atm}) - \mu^*_{\text{D, LIQ}}(T, p^*_D)$$
$$= \mu_{\text{D, VAP}}(T, p_D) - \mu_{\text{D, VAP}}(T, p^*_D)$$

This equation is the integrated form of

$\int d\mu_{\text{LIQ}} = \int d\mu_{\text{VAP}}$

Since $d\boldsymbol{G} = V dp - \boldsymbol{S} dT$, $(\partial\mu/\partial p)_T = V_m$

so that $\int d\mu_{\text{LIQ}} = \int d\mu_{\text{VAP}}$ becomes

$\int V_{m\,\text{LIQ}}\, dp = \int V_{m\,\text{VAP}}\, dp$

LHS integrated

from $p^*_D = 0.6$ atm

to $p_{tot} = p_D + p_E = 200$ atm

RHS integrated from $p^*_D = 0.6$ atm to p_D

LHS = $V_{m\,\text{D, LIQ}}(p_{tot} - p^*_D)$

<u>If</u> the vapor behaves ideally, then

RHS = $\int V_{m\,\text{D, VAP}}\, dp = \int RT\, dp/p$
$= RT \ln(p_D/p^*_D)$

$$V_{m\,\text{D, LIQ}}(p_{tot} - p^*_D) = RT \ln(p_D/p^*_D)$$

$V_{m\,D,\,LIQ}\,(200-0.6) = RT\,\ln(p_D/0.6)$

$(1/55)(200-0.6)$

$= (0.082057)(298)\,\ln(p_D/0.6)$

Solve for p_D,

$p_D = 0.696$ atm **Answer**

❀ $\mu_{CO2\ in\ solution}\,(278\ K,\ x_{CO2} = 0.001,\ p_{CO2})$

$= \mu_{CO2\ GAS}(278\ K,\ p_{CO2})$

Henry's law: $p_{CO2} = x_{CO2}\,K_H$

$p_{CO2} = (0.001)(1.25\times10^6) = 1250$ atm

Answer

❀ $\mu_{H2O,\ LIQ}(373\ \mathrm{K},\ p = 1\ \mathrm{atm})$
$= \mu_{H2O,\ VAP}(373\ \mathrm{K},\ p = 1\ \mathrm{atm})$

❀ $d\mu_{LIQ} = d\mu_{VAP}$,

as derived in problem 2, this leads to Clapeyron eq.

$$\ln (p/1\ \mathrm{atm}) \approx \Delta_{vap}\boldsymbol{H}/R \left[-\frac{1}{T} + \frac{1}{T_b} \right]$$

$$\ln (0.20 \mathrm{x} 0.987/1\ \mathrm{atm}) \approx (40.7 \times 10^3/8.3144) \left[-\frac{1}{T} + \frac{1}{373} \right]$$

solve for T

$T = 332\ \mathrm{K}$ Answer

EXAMPLE:

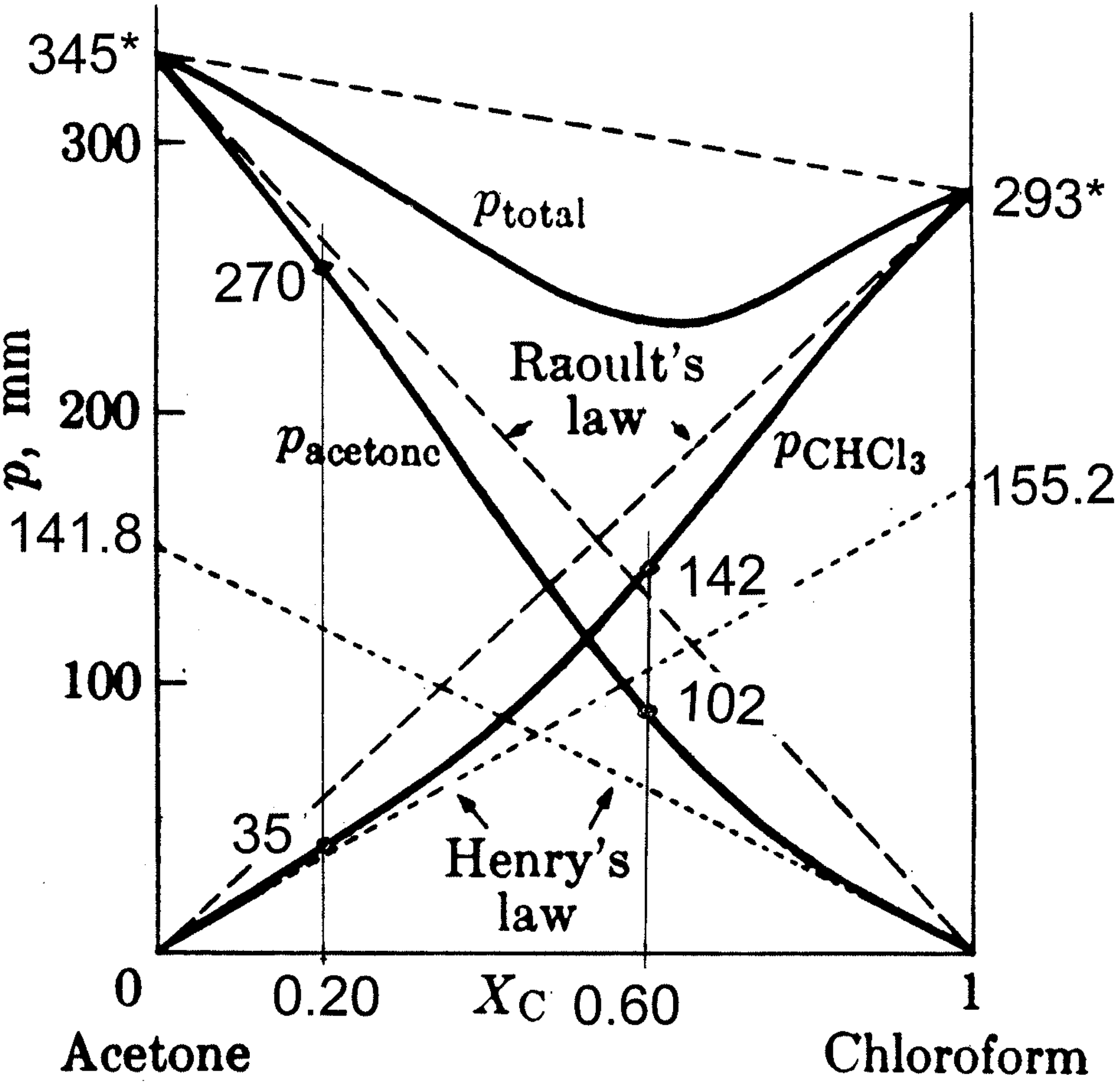
Calculate the ***activities*** a ***and activity coefficients*** γ ***in the rational system*** for the acetone-chloroform solution

$K_{H,C}$	from p_C data at $x_C < 0.10$	141.8
$K_{H,A}$	from p_A data at $x_A < 0.10$	155.2

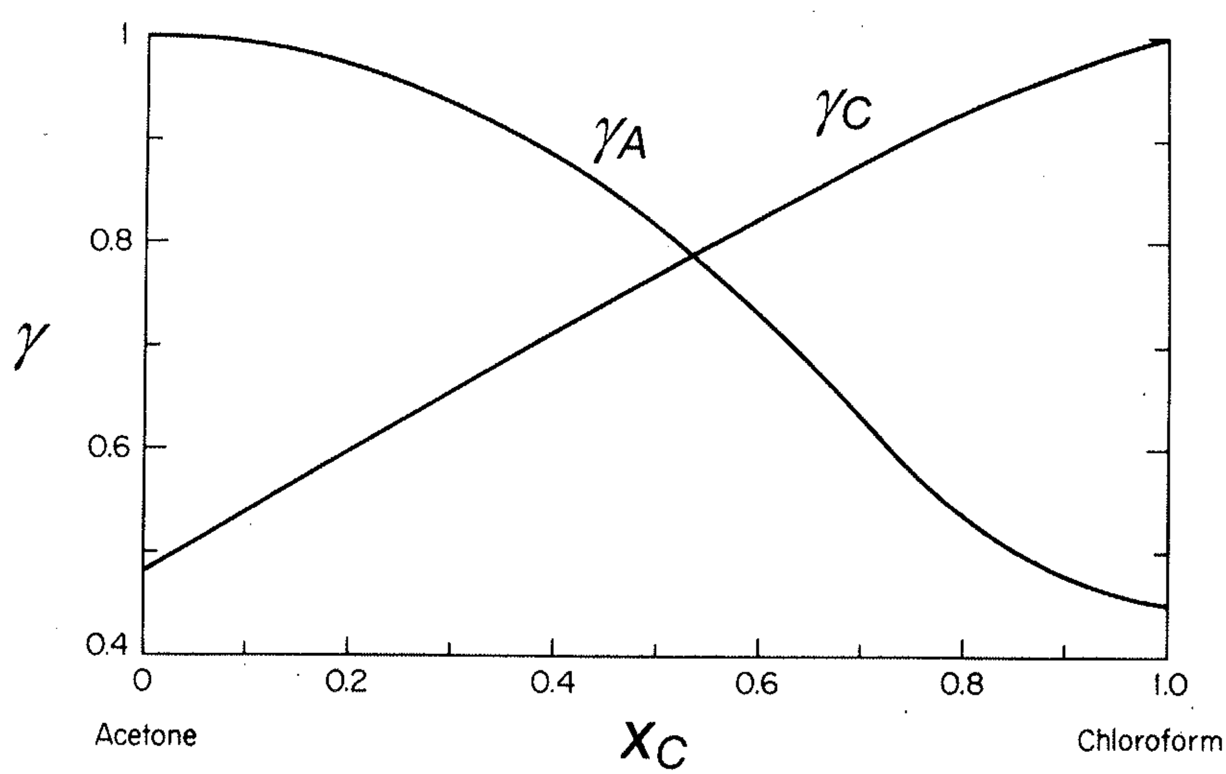
x_C	*given*	0.0	0.20	0.60	1.00
p_C	*given*	$x_C K_{HC}$	35	142	293*
p_A	*given*	345*	270	102	$x_A K_{HA}$

we get:

		for $x_C = 0.0$	$x_C = 0.20$	$x_C = 0.60$	$x_C = 1.00$
a_C	$= p_C / p^*_C$	0	0.120	0.485	1.00
a_A	$= p_A / p^*_A$	1.00	0.782	0.296	0
$p_{C,ideal}$	$x_C\, p^*_C$	0	59	176	293
$p_{A,ideal}$	$x_A\, p^*_A$	345	276	138	0
$\gamma_C = \dfrac{a_C}{a_{C,ideal}}$	$= a_C / x_C$ or $p_C / x_C\, p^*_C$	0.484	0.595	0.809	1.00 ideal in C
$\gamma_A = \dfrac{a_A}{a_{A,ideal}}$	$= a_A / x_A$ or $p_A / x_A\, p^*_A$	1.00 ideal in A	0.978	0.740	0.450



345*
300
200
141.8
100
p, mm
293*
155.2
270
142
102
35
p_total
Raoult's law
p_acetone
p_CHCl3
Henry's law
0
0.20
X_C
0.60
1
Acetone
Chloroform



1
0.8
0.6
0.4
γ
γ_A
γ_C
0
0.2
0.4
0.6
0.8
1.0
Acetone
x_C
Chloroform