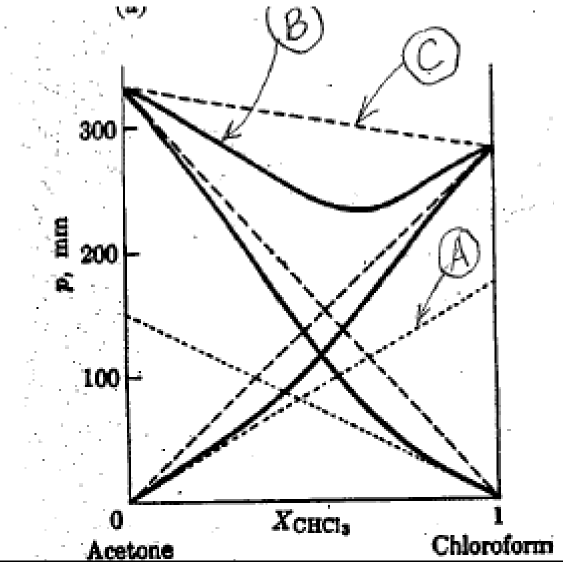
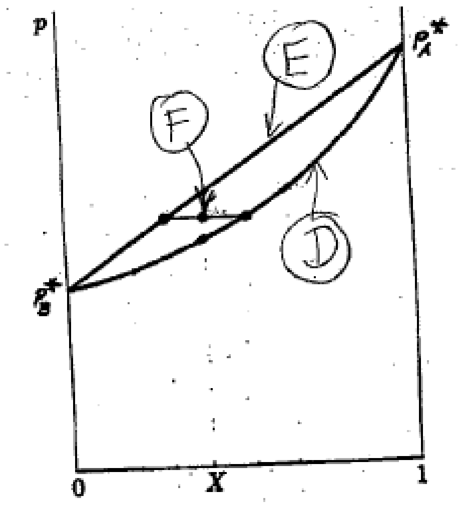
Solutions to Problem Set 9

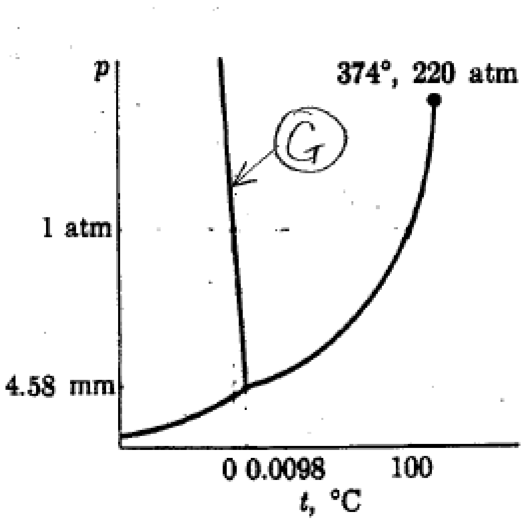
1. When possible, we want to write an equation with the quantity on the ordinate in terms of the quantity on the abscissa for each pf the labeled curves.



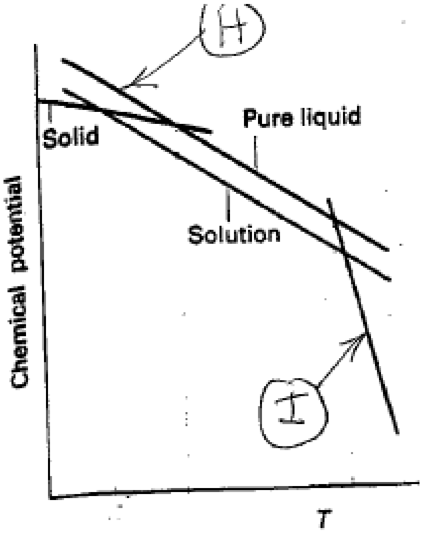
A	$p_{CHCl3} = K_H\ x_{CHCl3}$ where p_{CHCl3} is the partial pressure of $CHCl_3$ in the vapor of a solution obeying Henry's law with Henry's law constant of K_H and x_{CHCl3} is the mole fraction of CHCl3 in the liquid solution.
B	$p_{tot} = p_{acetone} + p_{CHCl3}$ This is the equation of the total vapor pressure p_{tot} over a real solution of acetone and chloroform, which is a simple sum of the partial pressures of the individual components in the vapor phase are $p_{acetone}$ and p_{CHCl3} . That is, Dalton's law of partial pressures still holds in the vapor even though the liquid solutions do not behave ideally. $p_{acetone}$ is a function of $(1-x_{CHCl3})$ and $\gamma_{acetone}$ obtained experimentally as a function of $1-x_{CHCl3}$), and p_{CHCl3} is a function of x_{CHCl3} and γ_{CHCl3} obtained experimentally as a function of x_{CHCl3},
C	$p_{tot} = (1-x_{CHCl3})\ p^*_{acetone} + x_{CHCl3}\ p^*_{CHCl3} = p^*_{acetone} + (p^*_{CHCl3} - p^*_{acetone})x_{CHCl3}$ This is the equation of the total vapor pressure p_{tot} over a solution obeying Raoult's law throughout the range of compositions, where x_{CHCl3} is the mole fraction of $CHCl_3$ and the vapor pressures of the pure components are $p^*_{acetone}$ and p^*_{CHCl3}



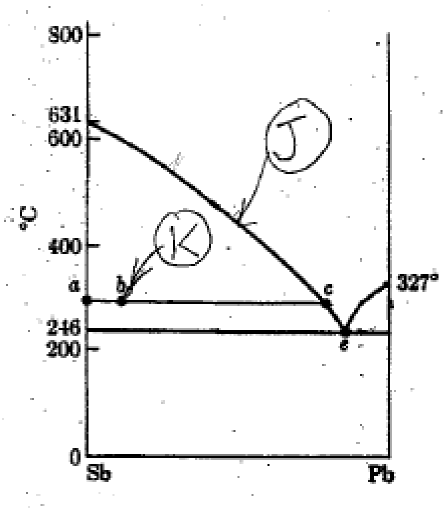
D	$p_{tot} = p^*_A p^*_B/\{ p^*_A + (p^*_A - p^*_B)y_A\}$ This curve is the Equation of the total vapor pressure p_{tot} over a solution in terms of the mole fraction y_A of component A in the vapor phase. We derive it as follows: $p_{tot} = p_A / y_A$ This relates p_{tot} and y_A but we want an expression that is in terms of p^*_A p^*_B and y_A. So start with this: $y_A = p_A/(p_A+p_B) = p^*_A x_A/\{p^*_A x_A+(1-x_A)p^*_B\}$. Now rearrange this so as to have x_A in terms of y_A: $x_A = p^*_B y_A/ \{ p^*_A + (p^*_B - p^*_A)y_A\}$ As in the Eq for E, $p_{tot} = p^*_B + (p^*_A - p^*_B)x_A$ where we now substitute our expression for x_A in order to have the desired equation in terms of y_A. $p_{tot} = p^*_B + (p^*_A - p^*_B)\bullet p^*_B \bullet y_A/ \{ p^*_A + (p^*_B - p^*_A)y_A\}$ Regroup terms to get $p_{tot} = p^*_A p^*_B/\{ p^*_A + (p^*_A - p^*_B)y_A\}$ which is not a straight line
E	$p_{tot} = x_A p^*_A + (1-x_A)p^*_B = p^*_B + (p^*_A - p^*_B)x_A$ This is the equation (like Line C above) of the total vapor pressure p_{tot} over a solution obeying Raoult's law throughout the range of compositions, where the equation is expressed and plotted in terms of the mole fraction x_A of component A and $(1-x_A)$ is the mole fraction component B, and the vapor pressures of the pure liquids are p^*_A and p^*_B. We know that the solution obeys Raoult's law because the line is a straight line connecting the vapor pressures of pure A and pure B.
F	$p_{tot} = \text{constant} = x_A p^*_A + (1-x_A)p^*_B = p_A / y_A$ This tie line is a line of *constant total vapor pressure* p_{tot} (thus a horizontal line) which extends between the values of x_A on line E and y_A on curve D. p_{tot} is a function of the overall composition z_A, such that (z_A-x_A) and (y_A-z_A) are the two line segments which are related to the relative amounts of liquid and vapor respectively. $(z_A-x_A) \bullet n_L = (y_A-z_A) \bullet n_V$ as derived in lecture notes part 8.



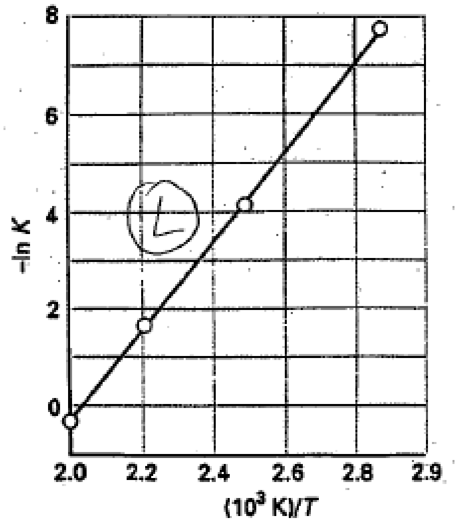
G	$dp/dt = (\mathbf{S}_{solid}-\mathbf{S}_{liq})/(V_{solid}-V_{liq}) \approx$ constant. The constant (slope) is negative (unusual) in this example, indicating that for this substance $V_{solid}-V_{liq} > 0$. This is the equation which describes the set of pressure p and temperature t values at which solid and liquid can coexist in equilibrium. **S** and V are the molar entropies and molar volumes for the solid and liquid phases.



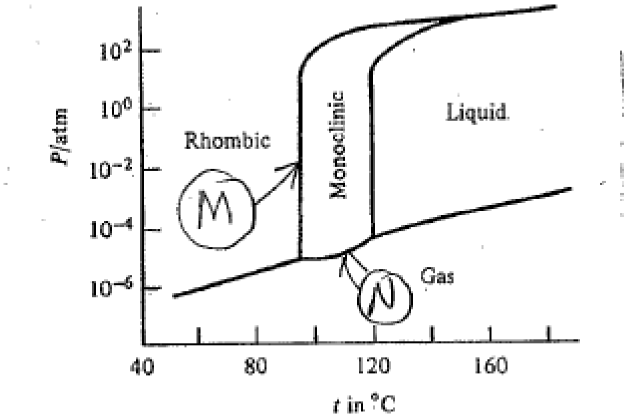
H	$d\mu_{liquid}/dT = -\mathbf{S}_{liquid}$ where μ_{liquid} is the chemical potential (molar Gibbs free energy) of a pure liquid at a given pressure, is a function of temperature such that the slope is the molar entropy $\mathbf{S}_{liquid}$. This follows directly from one of the fundamental equations of thermodynamics $d\mathbf{G} = Vdp - \mathbf{S}dT$, when examined at constant p for one mole of a pure substance
I	$d\mu_{vapor}/dT = -\mathbf{S}_{vapor}$ As above, except for the vapor phase.



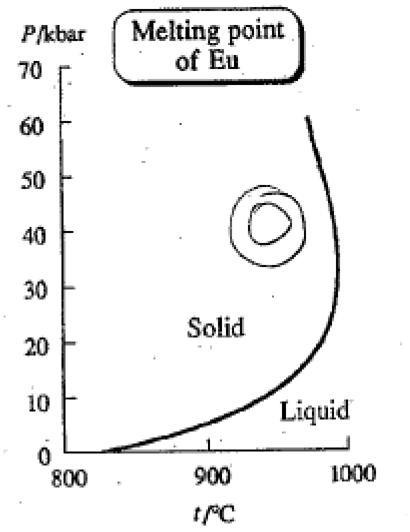
J	This is the equation of the freezing point of Sb which becomes depressed when solute Pb is introduced to form the solid solution of Sb and Pb. The equation of this curve of T vs x_{Pb} is a rearranged form of $\ln x_A = \Delta_{fus} \boldsymbol{H}/R \left[-\frac{1}{T} + \frac{1}{T^*} \right]$ where x_A is x_{Pb}, $T^* = 631 + 273$, $\Delta_{fus}\mathbf{H}$ = the molar enthalpy of fusion of Sb in J mol^{-1}, R is the gas constant 8.3145 J mol^{-1} K^{-1}.
K	T = constant At this specific temperature, the freezing point of the solution of Sb and Pb, pure Sb freezes out of a solid solution such that the mole fraction of Pb in the solution phase is given by the x coordinate of point c. The x coordinate of point a is of course zero mole fraction for Pb, that is, pure Sb



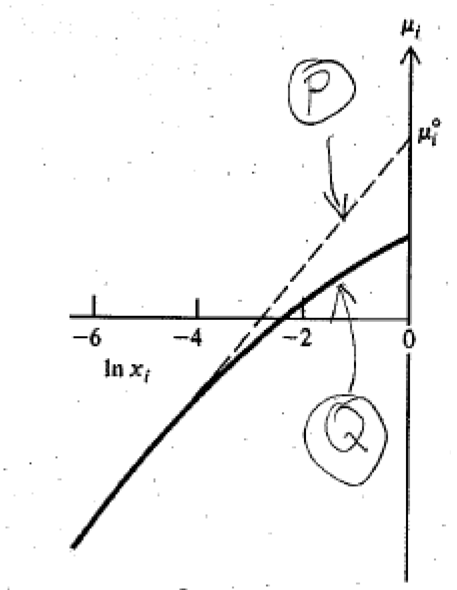
L	$\ln K(T_2) - \ln K(T_1) = -(1/R)\,\Delta_{rxn}\mathbf{H}^{\ominus}(T_1)\,\{T_2^{-1} - T_1^{-1}\}$ (Eq L) This comes from $\Delta_{rxn}\boldsymbol{G}^{\ominus}{}_{T} = -RT \ln K_p$ When Gibbs-Helmholtz relation is used, (see problem 5 below) $d \ln K / dT = \Delta_{rxn}\boldsymbol{H}^{\ominus}/RT^2$ Integration gives $\int d \ln K = (1/R)\int \Delta_{rxn}\mathbf{H}^{\ominus}(T)T^{-2}dT$ When $\Delta_{rxn}\mathbf{H}^{\ominus}$ is nearly independent of T, then the integrations leads to this Eq (L).



M	$dp/dT = (\mathbf{S}_{rhombic} - \mathbf{S}_{monoclinic})/(V_{rhombic} - V_{monoclinic})$ This curve is the equation for the set of (p,t) points for which $\mu_{solid,rhombic}(t,p) = \mu_{solid,monoclinic}(t,p)$ that is, the Clapeyron equation for the pressure and temperatures at which monoclinic and rhombic solids are in equilibrium
N	$dp/dT = (\mathbf{S}_{vap} - \mathbf{S}_{mono})/(V_{vap} - V_{mono})$ This curve is the equation for the set of (p,t) points for which $\mu_{vapor}(t,p) = \mu_{solid,monoclinic}(t,p)$ that is, the Clapeyron equation for the vapor pressure of the monoclinic solid at various temperatures.

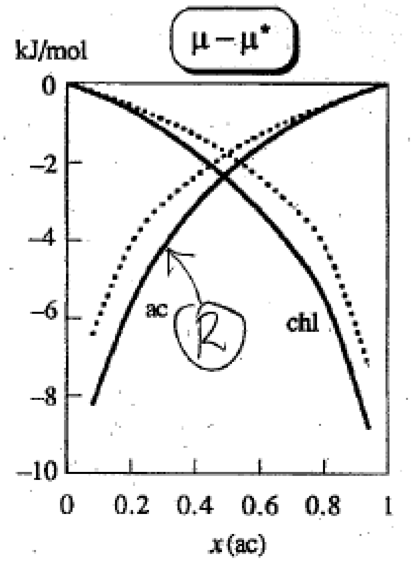


O	$dp/dT = (\mathbf{S}_{liquid} - \mathbf{S}_{solid}) / (V_{liquid} - V_{solid})$ This curve is the equation for the set of (p,t) points for which $\mu_{liquid}(t,p) = \mu_{solid}(t,p)$ that is, the Clapeyron equation for the freezing temperatures of the Eu at various temperatures



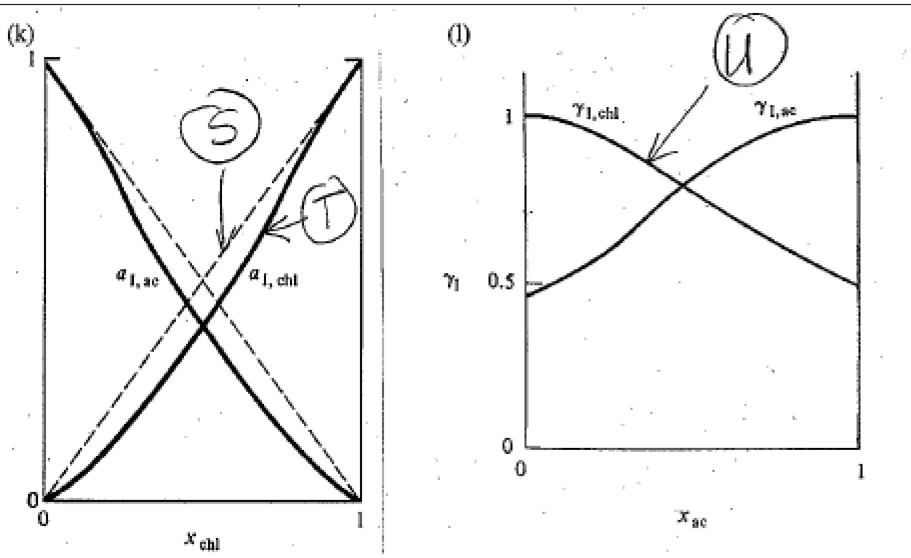
for a typical
nonelectrolyte solute.

P	$\mu_{i,T} = \mu^{\ominus}_{i,T}$ + RT lnx_i for a solute i in H_2O for example For a ”non-volatile” solute in an ideal solution $\mu_{solute,T} = \mu^{\ominus}_{solute,T}$ + RT ln a_{solute} where $\mu^{\ominus}_{solute,T}$ is the chemical potential of a *fictitious* *Henry’s law solution* having $p_{solute} = K_H$. This is why the $\mu^{\ominus}_{i,T}$ in this plot is not on the real curve of data. On the other hand, as $x_i \rightarrow 0$, $a_i \rightarrow x_i$, $\gamma_i = a_{i\,inH2O} / x_{i\,inH2O} \rightarrow 1$ (ideal) and the real data in Q becomes the same as the ideal in the limit of the ultra-dilute solution (large negative values for the ln x_i)
Q	$\mu_{i,T} = \mu^{\ominus}_{i,T}$ + RT lna_i for a solute i in H_2O where $a_i = \gamma_i \bullet x_i$ and γ_i changes with x_i as described above. This equation describes the real solution and becomes the same as the ideal equation P in the limit of the ultra-dilute solution at large negative values of ln x_i



acetone--chloroform solutions at 35°C and 1 atm.

R	$\mu_{acetone,T} - \mu_{acetone,T}^* = RT\ln a_{acetone}$ where $a_{acetone} = p_{acetone}/p^*_{acetone} = \gamma_{acetone} \bullet x_{acetone}$ Incidentally, the other curve for chloroform is $\mu_{CHCl3,T} = \mu_{CHCl3,T}^* + RT\ln a_{CHCl3}$ where $a_{CHCl3} = p_{CHCl3}/p^*_{CHCl3}$

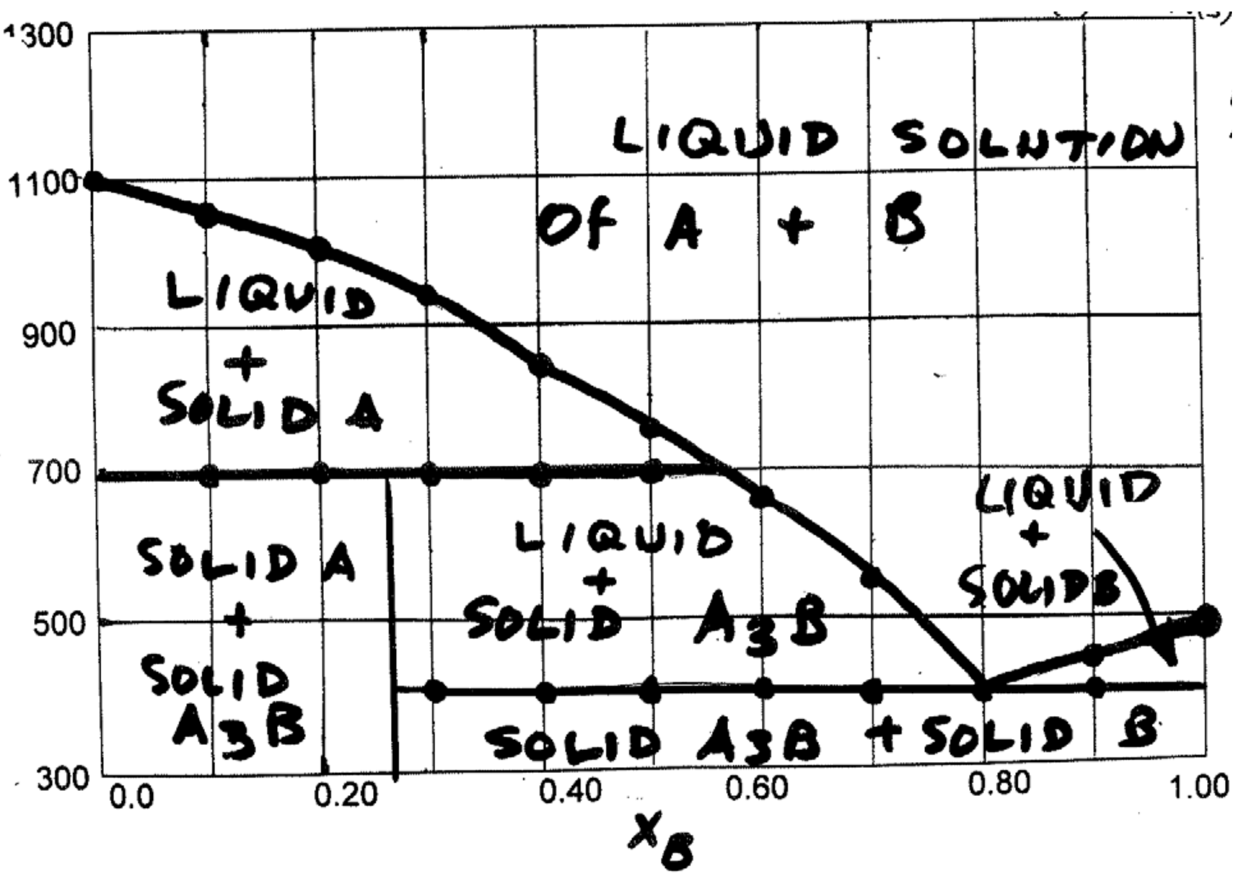


acetone-chloroform solutions at 35°C

S	$a_{CHCl3,\ ideal} = x_{CHCl3}$
T	$a_{CHCl3} = p_{CHCl3}/\ p^*_{CHCl3} = x_{CHCl3}\ \gamma_{CHCl3}$ This is not a straight line because the activity coefficient γ is not a linear function of x

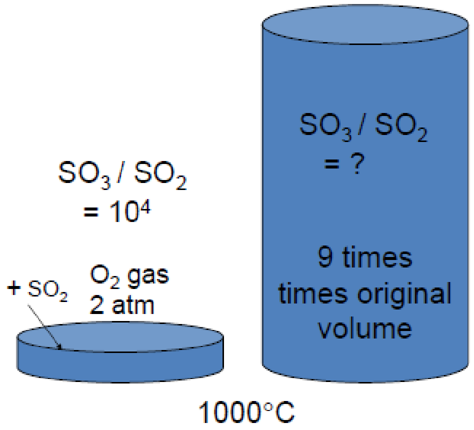
U	$\gamma_{\mathrm{CHCl3}} = a_{\mathrm{CHCl3}} / x_{\mathrm{CHCl3}}$ At one end of the curve, in the limit of $x_{\mathrm{acetone}} = 0$, it is pure $\mathrm{CHCl_3}$ so $\gamma_{\mathrm{CHCl3}} = a_{\mathrm{CHCl3}} / x_{\mathrm{CHCl3}}$ where $x_{\mathrm{CHCl3}} =1$ and $a_{\mathrm{CHCl3}} =1$, so $\gamma_{\mathrm{CHCl3}} = 1$ here. At the other end of the curve, x_{acetone} approaches 1, x_{CHCl3} approaches 0. At this limit, Henry's law holds for $\mathrm{CHCl_3}$, so $p_{\mathrm{CHCl3}} = K_H x_{\mathrm{CHCl3}}$ $a_{\mathrm{CHCl3}} = p_{\mathrm{CHCl3}}/ p^*_{\mathrm{CHCl3}}$ so at this limit, $a_{\mathrm{CHCl3l}} = K_H x_{\mathrm{CHCl3}}/ p^*_{\mathrm{CHCl3}}$. Since $\gamma_{\mathrm{CHCl3}} = a_{\mathrm{CHCl3}} / a_{\mathrm{ideal}}$, and $a_{\mathrm{ideal}} = 1$, then at this limit, $\gamma_{\mathrm{CHCl3}} = K_H x_{\mathrm{CHCl3}}/ p^*_{\mathrm{CHCl3}}$, a value close to 0.5

2.



Assume simplest formula for compound A_3B which melts incongruently at 700°C undergoing the peritectic reaction $A_3B(s) \rightarrow A(s)$ + LIQUID of composition $x_B = 0.57$

3. $SO_2(g) + \frac{1}{2}O_2(g) \Leftrightarrow SO_3(g)$



Equation	Basis for the equation	Eq. #
After equilibrium is reached: $p_{SO3}/p_{SO2} = 10^4$ $p_{O2} \approx 2$ atm p total ≈ 2 atm $K_p = \dfrac{p_{SO3}}{p_{SO2}\, p_{O2}{}^{1/2}}$ $K_p = 10^4/1.414 = 7071.$	Since only a small amount of SO_2 was introduced, the moles of O_2 is nearly unchanged Note: actually every partial pressure in the K_p expression to the left is implicitly divided by 1 atm in order to keep the quantity K_p dimensionless.	1 2
$7071 = \dfrac{p_{SO3}}{p_{SO2}\, p_{O2}{}^{1/2}} = \dfrac{p_{SO3}}{p_{SO2}\,(2/9)^{1/2}}$	Applying Eq 1 and new volume is 9V	3
$p_{SO3}/p_{SO2} = 3333$ **Answer**	Solving for p_{SO3}/p_{SO2}	4

4. $N_2O_4(g) \Leftrightarrow 2NO_2(g)$ degree of dissociation?

Equation	Basis for the equation	Eq. #
$\mathbf{G}^{\ominus}(N_2O_4, g) = 98.296$ kJ mol^{-1} $\mathbf{G}^{\ominus}(NO_2, g) = 51.8456$ kJ mol^{-1} $\Delta_{rxn}\mathbf{G}^{\ominus}$ for $N_2O_4(g) \Leftrightarrow 2NO_2(g)$ $= 2\,\mathbf{G}^{\ominus}(NO_2,g) - \mathbf{G}^{\ominus}(N_2O_4,g)$ $= 5.3952$ kJ mol^{-1}	Given at 298 K	
$\Delta_{rxn}G^{\ominus}_T = -RT \ln K_p$ 5395.2 J mol^{-1} $= -(8.31451$ J K^{-1} mol^{-1}) 298 ln K_p	Derived using $\mu = \mu^{\ominus} + RT \ln(p/1atm)$ for ideal gases, applied to reactants and products and setting $\Delta\mathbf{G} = 0$ at equilibrium	

$\ln K_p = -2.1775$ $K_p = 0.1133$	As noted above, every partial pressure quantity in the K_p expression is implicitly divided by 1 atm or 1 bar which insures that K_p is dimensionless	
(a) $p_{tot} = 2$ atm Let degree of dissociation is x $p_{N2O4} = p_{tot}\bullet(1-x)/(1+x)$ $p_{NO2} = p_{tot}\bullet(2x)/(1+x)$ Here $K_p = (p_{NO2})^2/p_{N2O4}$ $0.1133 = \frac{[2x/(1+x)]^2 \bullet 2}{(1-x)/(1+x)}$ $\frac{0.1133}{8} = \frac{x^2}{(1-x^2)}$	given Assuming Dalton's law of partial pressures is valid, as for ideal gases Note that the total moles of N_2O_4 at the start being any number n instead of 1 does not affect the degree of dissociation because all moles, including total moles are mutiplied by n, so n drops out in taking the mole fraction of each component.	
x = 0.118 **Answer**	Solving for x	
(b) ptot = 2 atm including 5 mol Ar Let degree of dissociation is x This time we need to look at total moles since Ar contributes to it moles $N_2O_4 = 2(1-x)$ moles $NO_2 = 2(2x)$ total moles = 2(1+x) + 5 = 7+2x $p_{N2O4} = p_{tot}\bullet 2(1-x)/(7+2x)$ $p_{NO2} = p_{tot}\bullet 2(2x)/(7+2x)$ Here $K_p = (p_{NO2})^2/p_{N2O4}$ $0.1133 = \frac{[4x/(7+2x)]^2 \bullet 2}{2(1-x)/(7+2x)}$ $0.1133 = \frac{16x^2}{7-5x-2x^2}$. $16.2266x^2 + 0.5665x - 0.7931 = 0$ x = 0.204 **Answer** (the other root leads to negative and unphysical degree of dissociation so discard it)	Substitute partial pressures into K_p Note that this is somewhat larger than in the absence of added Ar	
(c) original volume kept constant then add 5 moles Ar V = 2 mol 298R /2 atm = 298 R total moles = 7+2x as shown above, also partial pressures as shown above p_{tot} (298 R) = (7+2x) 298 R $p_{tot} = (7+2x)$ $0.1133 = \frac{[4x/(7+2x)]^2 \bullet (7+2x)}{2(1-x)/(7+2x)}$ $0.1133 = \frac{8x^2}{(1-x)}$	Using ideal gas law Using ideal gas law Substitute into K_p	

x = 0.112 **Answer** similarly discard unphysical negative value of x	Note that this is less than in absence of added Ar With the volume kept constant, LeChatelier's principle predicts that equilibrium will shift toward fewer particles (fewer NO_2) to relieve the stress of additional non-reacting (Ar) particles introduced into the same volume.	

5. $2NOBr(g) \Leftrightarrow 2NO + Br_2(g)$ $K_{600K} = ?$

Equation	Basis for the equation	Eq. #
$\Delta_{rxn}\mathbf{H}^{\ominus}$ for the reaction at 300 K and 1 bar pressure = 15.7 kcal $K_p = 0.035$ at 300 K	Given Given	
For any temperature T, we need to correct this value by using $(\partial\mathbf{H}/\partial T)_p\, dT$ integrated from 300 to T $\Delta_{rxn}\mathbf{H}^{\ominus}(T) = 15.7 \text{ kcal mol}^{-1}$ $+\int_{300}^{T} [C_p(Br_2) + 2C_p(NO)$ $- 2\,C_p(NOBr)]\, dT$		1
$\Delta_{rxn}\mathbf{H}^{\ominus}(T) = 15700$ $+\int_{300}^{T}[8.6 + 2(7.0) - 2(6.3)]dT$ $\Delta_{rxn}\mathbf{H}^{\ominus}(T) = 15700 + 10(T-300)$ $= 12700 + 10T$	We were allowed to assume that all C_p in this problem are almost independent of temperature in this temperature range. $\Delta_{rxn}\mathbf{H}^{\ominus}(600) = 18700$ cal mol^{-1}	2
: $(\partial(\Delta \mathbf{G}/T)/\partial T)_p = -(\Delta \mathbf{H}/T^2)$	From the definition **G** = **H** -T**S**, or (**G**/T)= (**H**/T) -**S**, we easily derive the Gibbs-Helmholtz relation.	3
$\Delta_{rxn}\mathbf{G}^{\ominus}_{T}/T = -R\ln K$	Derived using $\mu = \mu^{\ominus} + RT\ln(p/1\text{atm})$ for ideal gases, applied to reactants and products and setting $\Delta\mathbf{G} = 0$ at equilibrium	4
$d\ln K/dT = \Delta_{rxn}\mathbf{H}^{\ominus}/RT^2$	When we apply the Gibbs-Helmhotz relation to $\Delta_{rxn}\mathbf{G}^{\ominus}$ chemical reaction in Eq 4	5
$R\, d\ln K = \Delta_{rxn}\mathbf{H}^{\ominus}(T)T^{-2}dT$	Rearranging Eq 5	6
$R\int d\ln K = \int \Delta_{rxn}\mathbf{H}^{\ominus}(T)T^{-2}dT$ $= \int [12700 + 10T]\, T^{-2}dT$ $= 12700\,[T^{-1} - 300^{-1}] + 10\ln(T/300)$	Substituting Eq 2 into Eq 6 and integrating	7
$R\ln(K_{600}/K_{300}) = 12700\,[600^{-1} - 300^{-1}]$ $+10\ln(600/300)$ $\ln(K_{600}/0.035)$ $= [-21.1666 + 6.93]/1.9872$ $= -7.164$ $K_{600}/0.035 = \exp(-7.164) = 0.000774$ $K_{600} = 2.709\times10^{-5}$ **Answer**	Applying Eq 7 at upper limit of T = 600 K	

6. ideal gases $2NO_2(g) \rightarrow N_2O_4(g)$

(a) $\Delta_{rxn}\mathbf{H}^{\ominus}$ for the reaction at 298.15 K and 1 bar pressure = $\mathbf{H}^{\ominus}(N_2O_4)$- $2\mathbf{H}^{\ominus}(NO_2)$
= 9.16 - 2(33.18) kJ mol^{-1}, using values at 298.15 K and 1 bar pressure from
Appendix A (per instructions for this problem)
= - 57.20 kJ mol^{-1}

$\Delta_{rxn}\mu^{\ominus}$ for the reaction at 298.1 K and 1 bar pressure = $\mu^{\ominus}(N_2O_4)$- $2\mu^{\ominus}(NO_2)$
= 97.89 - 2(51.31) kJ mol^{-1}, using values at 298.15 K and 1 bar pressure from
Appendix A (per instructions for this problem)
= - 4.73 kJ mol^{-1}

(b) f / p = 1 for an ideal gas, so fugacity is p for $NO_2(g)$ at 298.15 K and p = 1 to 400 bar

(c) K_p for the reaction can be obtained from $\Delta_{rxn}\boldsymbol{G}^{\ominus}{}_T = -RT \ln K_p$
$\Delta_{rxn}\mu^{\ominus}$= - 4.73 kJ mol^{-1} = - RT ln K_p
K_p = exp [4730 J mol^{-1} / (8.31451 J $mol^{-1}K^{-1}$)298.15K] = exp (1.908) = 6.740

For mixtures, the activity of a component of a gas, for example N_2O_4 is, $a_{N2O4} = p_{N2O4}/p^{\ominus}$

$$K_p = \frac{p_{N2O4}/p^{\ominus}}{(p_{NO2}/p^{\ominus})^2}$$

p_{NO2} and p_{N2O4} are partial pressures. The inclusion of the terms in the standard pressure

$p^{\ominus}$ = 1 bar = 10^5 Pa, 1 atm = 1.01325 bar, close enough to old standard $p^{\ominus}$ = 1
(in this problem using 1 bar for standard pressure)
ensure that the activities are dimensionless, so that the equilibrium constant is also dimensionless and it is okay to take its natural log in

$$\Delta_{rxn}\boldsymbol{G}^{\ominus}{}_T = -RT \ln K_p$$

For activities in terms of concentrations,
$a_{N2O4} = [N_2O_4]/c^{\ominus}$
where the concentration $[N_2O_4]$ is in mol L^{-1},
and the standard concentration $c^{\ominus}$ is 1 mol L^{-1}

$$K_C = \frac{[N_2O_4]/c^{\ominus}}{([NO_2]/c^{\ominus})^2}$$

RT $[N_2O_4] = p_{N2O4}$, RT $[NO_2] = p_{NO2}$ **for ideal gases**

$$p^{\ominus}K_p = \frac{RT[N_2O_4]}{(RT)^2[NO_2]^2} = \frac{c^{\ominus}\ K_C}{RT}$$

In general,

$$(RT\,p^{\ominus})^{-\Delta n} K_p = (c^{\ominus})^{-\Delta n} K_C \text{ where } \Delta n = \text{products - reactants}$$

In this problem, $\Delta n = -1$, $RT\,p^{\ominus}K_p = c^{\ominus}\ K_C$

Note that RT $p^{\ominus}/c^{\ominus}$ = 0.0831451 L bar mol^{-1} K^{-1}•298.15 K• 1 bar / 1 mol L^{-1}
is dimensionless, as is the general case $(RT\,p^{\ominus}/c^{\ominus})^{-\Delta n}$, and also K_p and K_C are dimensionless, as they should be.

$K_C = K_p \bullet RT$ = 6.740• 0.0831451•298.15 = 167.08 at 298.15K

(d) $\Delta_{rxn}\mathbf{H}^{\ominus}$ for the reaction at 298.15K and 1 bar pressure = - 57.20 kJ mol^{-1} from part (a)
For any temperature T, we need to correct this value by using $(\partial\mathbf{H}/\partial T)_p\, dT$ integrated from 298.15 to T

$\Delta_{rxn}\mathbf{H}^{\ominus}(T) = -57.20 \text{ kJ mol}^{-1} + \int_{298}^{T} [C_p(N_2O_4) - 2\,C_p(NO_2)]\, dT$

using $C_p = 10.719 + 2.86\times10^{-2}T - 8.726\times10^{-6}T^2$ cal mol^{-1} K^{-1} for $N_2O_4(g)$

$C_p = 6.37 + 1.01\times10^{-2}T - 3.405\times10^{-6}T^2$ cal mol^{-1} K^{-1} for $NO_2(g)$

4.184 j = 1 cal

$$\begin{aligned}\Delta_{rxn}\mathbf{H}^{\ominus}(T) = {} & -57.20\times10^{3} \\ & + 4.184\{(10.719 - 2\bullet6.37)(T-298.1) + (1/2)[2.86-2\bullet1.01]\times10^{-2}[T^2 - (298.15)^2] \\ & - (1/3)[8.726-2\bullet3.405]\times10^{-6}[T^3 - (298.15)^3]\}\end{aligned}$$

$$= -57.20\times10^{3} - 8.456(T-298.1) + 1.757\times10^{-2}[T^2 - (298.15)^2] - 2.674\times10^{-6}[T^3 - (298.15)^3]$$

$$\Delta_{rxn}\mathbf{H}^{\ominus}(T) = -56.17\times10^{3} - 8.456T + 1.757\times10^{-2}T^2 - 2.674\times10^{-6}T^3 \text{ J mol}^{-1}$$

$$\Delta_{rxn}\mathbf{H}^{\ominus}(1000\text{ K}) = -56.17\times10^{3} - 8.456\times10^{3} + 17.57\times10^{3} - 2.674\times10^{3} = -49.73\times10^{3} \text{ J mol}^{-1}$$

(e) From the definition **G** = **H** -T**S**, or (**G**/T)= (**H**/T) -**S**, we easily derive the Gibbs-Helmholtz relation: $(\partial(\Delta\boldsymbol{G}/T)/\partial T)_p = -(\Delta\boldsymbol{H}/T^2)$
When we apply this relation to K_p

$$\Delta_{rxn}\boldsymbol{G}^{\ominus}_{T}/T = -R\ln K \text{ we get}$$

$$d\ln K/dT = \Delta_{rxn}\boldsymbol{H}^{\ominus}/RT^2$$

Using this equation & $\Delta_{rxn}\mathbf{H}^{\ominus}(T) = -56.17\times10^{3} - 8.456T + 1.757\times10^{-2}T^2 - 2.674\times10^{-6}T^3$ from above,

$R\,d\ln K = \Delta_{rxn}\mathbf{H}^{\ominus}(T)T^{-2}dT = \{-56.17\times10^{3}T^{-2} - 8.456T^{-1} + 1.757\times10^{-2} - 2.674\times10^{-6}T\}dT$

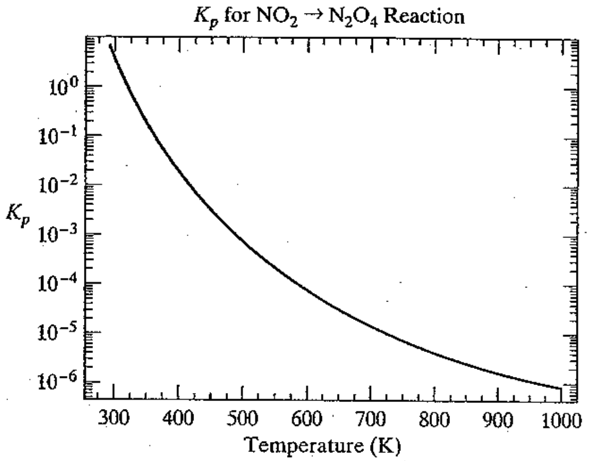
Integrating from 298.15 to T, we get for K_p as a function of temperature,

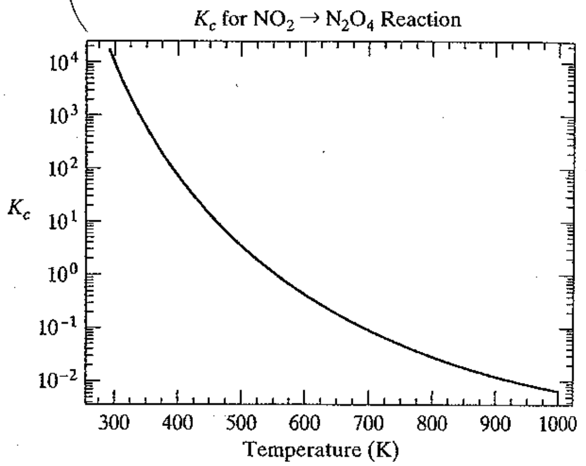
$$\begin{aligned}R\ln(K_T/K_{298}) = {} & -1(-56.17\times10^{3})[T^{-1} - 298.15^{-1}] - (8.456)\ln(T/298) \\ & + (1.757\times10^{-2})(T-298.15) - (1/2)(2.674\times10^{-6})(T^2 - 298.15^2)\end{aligned}$$

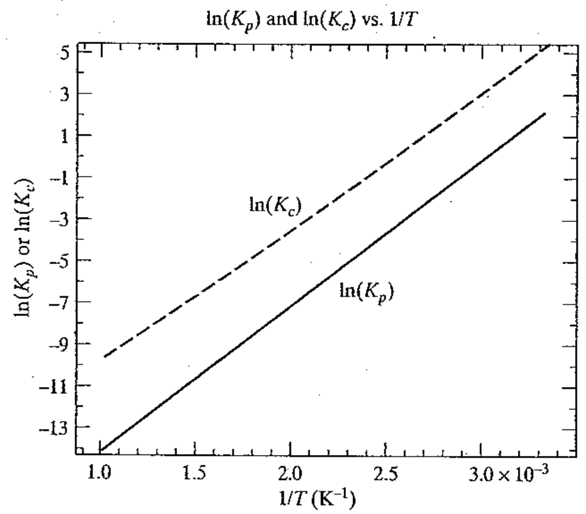
$$\ln(K_T/K_{298}) = -23.275 + 6.756\times10^{3}T^{-1} - 1.0170\ln(T/298) + 0.00211T - 0.1608\times10^{-6}T^2$$

Note that although there are several powers of T here, the dominant term is that of T^{-1}. Thus we expect that a plot of $\ln(K_T/K_{298})$ vs T^{-1} should be approximately a straight line.

We had already found $K_C = K_p \bullet RT$ for this reaction
$d \ln K_c/dT = d\ln K_p/dT + d\ln T/dT$
Integrating between the limits 298 K and T,
$\ln(K_{cT}/K_{c298}) = \ln(K_{pT}/K_{p298}) + \ln (T/298)$.
That is, we need to add ln(T/298) to the above expression, to get:
$\ln(K_{cT}/K_{c298}) = - 23.275 + 6.756\times10^3 T^{-1} - 0.0170 \ln(T/298) + 0.00211T - 0.1608\times10^{-6} T^2$
Note that although there are several powers of T here, the dominant term is that of T^{-1}
Thus we expect that a plot of $\ln(K_{cT}/K_{c298})$ vs T^{-1} should be approximately a straight line, too.
Ref.: Plots from L. M. Raff Solutions Manual Principles of Physical Chemistry


K_p for $NO_2 \rightarrow N_2O_4$ Reaction


K_c for $NO_2 \rightarrow N_2O_4$ Reaction


$\ln(K_p)$ and $\ln(K_c)$ vs. $1/T$

(f) $2NO_2 \Leftrightarrow N_2O_4$

initially:	1 mol/2L	0 mol/2L	in a sealed rigid container
Let all form N_2O_4	0 mol L^{-1}	0.25mol L^{-1}	
concentrations at equil	2x	0.25-x mol L^{-1}	

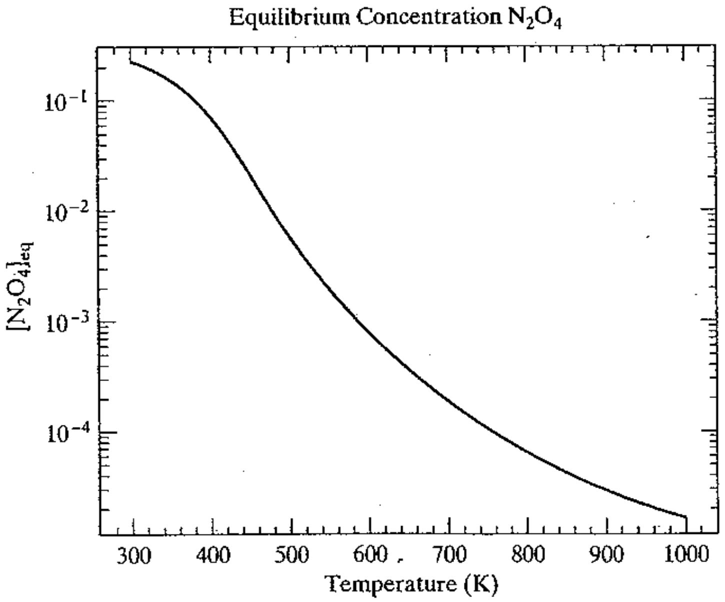
$$K_C = \frac{0.25-x\ .}{4x^2}$$

Note that we chose to use K_C to do the calculation rather than K_p because the problem said “sealed rigid container” (constant volume of 2 L) which means that the concentrations can be determined from the number of moles.
At 298 K, $167.08 = [0.25- x] /4x^2$
Note that the very large $K_C =$ 167.08 means that at 298 K nearly all the NO_2 goes to N_2O_4, so it is easier to solve the equation if start closer to the final condition, since then we can approximate $(0.25 - x) \approx 0.25$. At 298 K, $167.08 = [0.25- x] /4x^2 \approx 0.25/4x^2$ we find $x \approx 0.0193$
Using the quadratic formula: $167.08 = [0.25- x] /4x^2$ gives $x = 0.01861$
$[NO_2] = 0.0372$ mol L^{-1}, $[N_2O_4] = 0.25 - 0.01861 = 0.2314$ mol L^{-1}, total mol L^{-1} =0.2686

$\ln(K_{cT}/K_{c298}) = - 23.275 + 6.756\times10^3 T^{-1} - 0.0170 \ln(T/298) + 0.00211T - 0.1608\times10^{-6} T^2$

At 1000 K,
$\ln(K_{C1000}/K_{c298}) = -23.275 +6.756 - 0.0207 +2.11 - 0.1608 = - 14.59$
$4.61\times10^{-7} = K_{C1000}/K_{C298}$
$K_{C1000} = 7.73\times10^{-5}$
This is very small so equilibrium mixture has essentially zero N_2O_4.
Thus, N_2O_4 concentration drops from 0.2314 mol L^{-1} at 298 K to almost zero at 1000 K.

Ref.: Plot from L. M. Raff, Solutions Manual Principles of Physical Chemistry



(g) $$2NO_2 \Leftrightarrow N_2O_4$$

Given: Dalton's law of partial pressure holds. Then partial pressures add up to total pressure and are related to molefractions: $p_{N2O4} = X_{N2O4}\bullet p_{tot}$, $p_{NO2} = X_{NO2}\bullet p_{tot}$

How is total pressure involved?

K_p is a constant at a fixed temperature, in terms of the partial pressures at equilibrium

$$K_p = \frac{p_{N2O4}/p^{\ominus}}{(p_{NO2}/p^{\ominus})^2} = \frac{p_{tot}X_{N2O4}/p^{\ominus}}{(p_{tot}X_{NO2}/p^{\ominus})^2} = \frac{X_{N2O4}}{X_{NO2}^{2}(p_{tot}/p^{\ominus})}$$

$X_{NO2} = 1 - X_{N2O4}$

$K_{p\ 298.15\ K} = 6.740$

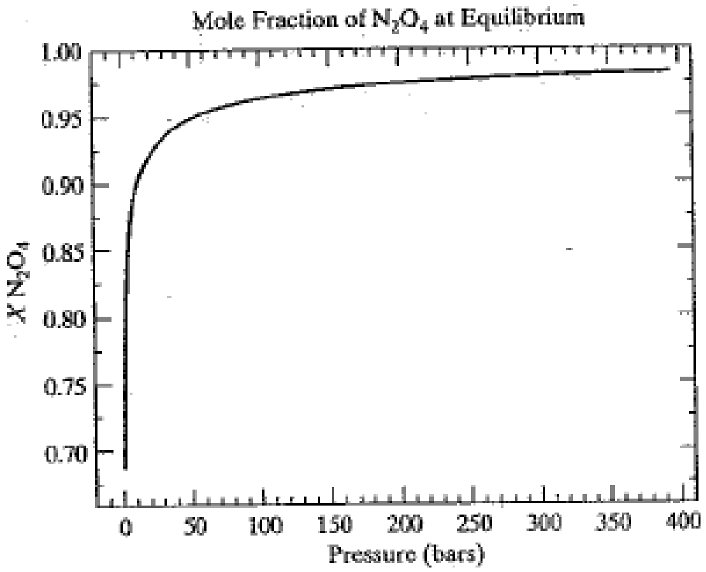
$(p_{tot}/p^{\ominus})\bullet 6.740 = X_{N2O4} / [1-X_{N2O4}]^2$

This is the relation between X_{N2O4} and p_{tot} . To put it in a more conventional form, we need to solve for X_{N2O4} as a function of p_{tot} .

$p^{\ominus} = 1$ bar: Solve $(p_{tot}/1\text{bar})\ 6.740 = X_{N2O4} / [1-X_{N2O4}]^2$ for the unknown X_{N2O4}

$$X_{N2O4} = \frac{(13.48p_{tot}+1) - [(13.48p_{tot}+1)^2 - 4(6.740)^2 p_{tot}^2]^{½}}{13.48p_{tot}}$$

Ref.: Plot from L. M. Raff, Solutions Manual Principles of Physical Chemistry



7. Now do the same as problem 6 but for non-ideal gas

Given equation of state:

$$pV = RT + B_1(T)p + B_2(T)\,p^2/RT$$

where $B_1(T) = b - a/RT$ and $B_2(T) = b^2$.
For $NO_2(g)$ $a = 5.354\ L^2\ bar\ mol^{-2}$, $b = 0.04424\ L\ mol^{-1}$, for $N_2O_4(g)$ $a = 6.550\ L^2\ bar\ mol^{-2}$, $b = 0.05636\ L\ mol^{-1}$. The heat capacities are the same as in problem 6.

What should we do differently for non-ideal gases?

(a) This is unchanged by the fact that the gases are assumed to be ideal because the quantities used from the Appendix, $\mathbf{H}^{\ominus}$ and $\mu^{\ominus}$ at 298.15 K and 1 bar, are experimental values for real gases.

(b) Fugacity:

$$\ln \frac{f}{p} = \int_0^p \frac{(V - V_{id})}{RT}\,dp$$

Replace V by $RT/p + b - a/RT + b^2\,p/RT$ and V_{id} by RT/p

$(V-V_{id}) = b - a/RT + b^2\,p/RT$

integral = $[RT]^{-1} \int_0^p (b-a/RT)dp + (b^2/RT)pdp = [RT]^{-1}\{ (b-a/RT)p + (1/2)(b^2/RT)p^2 \}$

for NO_2 : integral = $[0.0831451\ L\ bar\ mol^{-1}K^{-1}\ 298K]^{-1} \bullet 0.04424\ L\ mol^{-1}\ p$

$+ [0.0831451\ L\ bar\ mol^{-1}K^{-1}\ 298K]^{-2} \bullet \{ - 5.354\ L^2\ bar\ mol^{-2}\ p + 0.5[0.04424\ L\ mol^{-1}]^2\ p^2 \}$

Units all check out to leave dimensionless result, if p is in bars:

$\ln(f/p) = 0.04036 \bullet 0.04424p + 0.0016289 \bullet \{- 5.354p + 9.785\times10^{-4}p^2\}$

$= - 0.00693p + 1.594\times10^{-6}p^2$

$f/p = \exp[- 0.00693p + 1.594\times10^{-6}p^2]$ for NO_2

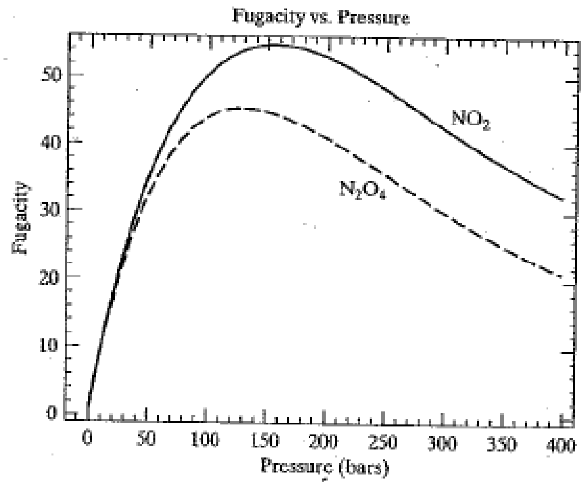
for N_2O_4: $\ln(f/p) = 0.04036 \bullet 0.05636p + 0.0016289 \bullet \{- 6.550p + 7.941\times10^{-4}p^2\}$

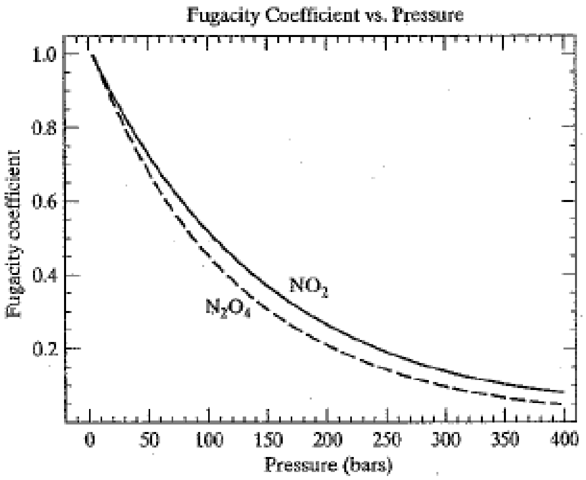
$= - 0.00839\ p + 1.29\times10^{-6}p^2$

$f/p = \exp[- 0.00839\ p + 1.29\times10^{-6}p^2]$

For p =1-400 bars, the negative term dominates and f/p is less than 1 (see plot below right).

Ref.: Plot from L. M. Raff, Solutions Manual Principles of Physical Chemistry





(c) The value of K_p derived from

$$\Delta_{rxn} G^{\ominus}_T = - RT \ln K_p$$

where K is in terms of ***activities*** does not depend on whether the gases are ideal.

The choice is to keep the same general relation $\Delta_{rxn} G^{\ominus}_T = - RT \ln K_p$ but make sure that the expression for K is constituted of activities, or fugacities in the case of gases. To be more explicit, we could write

$\Delta_{rxn} G^{\ominus} (T) = - RT \ln K_f$

This relation comes from

$$\mu(T) = \mu^{\ominus}_T \quad + \quad RT \ln \frac{f}{1} \quad \text{(real gas)}$$

instead of

$$\mu(T) = \mu^{\ominus}_T \quad + \quad RT \ln \frac{p}{1} \quad \text{(ideal gas)}$$

Use $K = \dfrac{p_{N2O4}/p^{\ominus}}{(p_{NO2}/p^{\ominus})^2}$ only for ideal gases

Use $K = \dfrac{f_{N2O4}/f^{\ominus}}{(f_{NO2}/f^{\ominus})^2}$ for non-ideal gases

Furthermore, the relation between K_C and K_p used in problem 6 no longer holds for non-ideal gases because we used $p = nRT/V$ to derive it. Furthermore non-ideal gases do not follow Dalton's law of partial pressures, since mole fractions depend only on numbers of molecules, but activities at a given mole fractions in a mixture also depend on total pressure.

(d) The temperature dependence of $\Delta_{rxn}\mathbf{H}^{\ominus}$ (T) obtained in problem 6 does not depend on assumed ideality of the gases, since the experimental heat capacities for real gases are the quantities used. Therefore, the answer in problem 6 is the same here for real gases.

(e) The temperature dependence of K_p derived from the general relation

$$\mathrm{d}\ \ln K / \mathrm{d}T = \Delta_{rxn}\boldsymbol{H}^{\ominus}/RT^2$$

is unchanged from problem 6 for the same reason as in (d), *provided we mean to use the fugacity expression for K*, but the relation between K_C and K_f is not the same as found in problem 6 for the relation between K_C and K_p where the ideal gas assumption was used to connect the two.

(f) The equilibrium concentration of N_2O_4 will be related to total pressure at each temperature because partial pressures in a gas mixture will depend on total pressure and composition in a way different from that for ideal gases.

(g) The dependence of the mole fraction of N_2O_4 on total pressure will be different from that obtained in problem 6. That is, we can no longer use the result

$(p/1\mathrm{bar})\ 6.740 = X_{N2O4} / [1-X_{N2O4}]^2$

to find the desired pressure dependence of mole fraction of N_2O_4 because we used Dalton's law of partial pressures for mixtures to derive this and when gases are non-ideal, Dalton's law strictly can no longer apply. The non-ideality comes from non-negligible interactions between molecules and these interactions depend not only on relative numbers of molecules of each kind but also the conditions (T and p) that these molecules are subjected to.