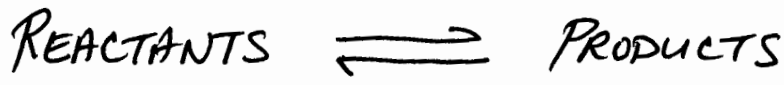


CHAPTER 13: CHEMICAL-REACTION EQUILIBRIA



- REACTION RATE
 - EQUILIBRIUM CONVERSION
- } ALL $f(T, P, n_i)$

• CATALYST

- INCREASES RATE OF REACTION
- NO EFFECT ON EQUILIBRIUM CONVERSION

• TEMPERATURE

- CAN AFFECT RATE AND EQUILIBRIUM CONVERSION.

HOW DOES THERMODYNAMICS PLAY A ROLE?

- ⇒ DOES NOT PREDICT RATE
- ⇒ DOES PREDICT EQUILIBRIUM CONVERSION

SO...

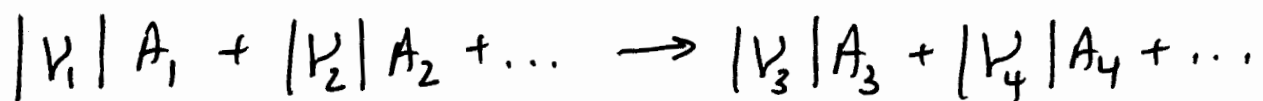
USE THERMODYNAMICS TO PREDICT EQUILIBRIUM
CONVERSION FIRST.

THEN,

IF ACCEPTABLE, THEN IT IS WORTH THE
EFFORT TO FIND A CATALYST + OPERATING
T, P, etc.

GETTING STARTED... REACTION COORDINATE...

13.1 THE REACTION COORDINATE



where $|v_i| \equiv$ Stoichiometric coefficient

$A_i \equiv$ Chemical formula

NOTE: SIGN ON STOICHIOMETRIC COEFFICIENT

(-) for reactant

(+) for product

EXAMPLE:



$$V_{\text{CH}_4} = -1$$

$$V_{\text{CO}} = +1$$

$$V_{\text{H}_2\text{O}} = -1$$

$$V_{\text{H}_2} = +3$$

NOTE: If there is an inert component

(such as N_2), $V_{\text{INERT}} = 0$

DURING REACTION, AS $\text{CH}_4 + \text{H}_2\text{O}$ DISAPPEAR,
 $\text{CO} + \text{H}_2$ ARE FORMED.

EXAMPLE: 0.5 mol CH_4 + 0.5 mol H_2O disappear

(4)

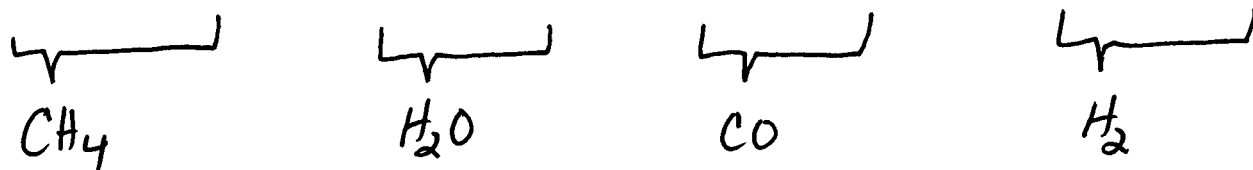
AND SIMULTANEOUSLY,

0.5 mol CO + 1.5 mol H₂ formed.

So,

$$\frac{\Delta n_{\text{CH}_4}}{\nu_{\text{CH}_4}} = \frac{\Delta n_{\text{H}_2\text{O}}}{\nu_{\text{H}_2\text{O}}} = \frac{\Delta n_{\text{CO}}}{\nu_{\text{CO}}} = \frac{\Delta n_{\text{H}_2}}{\nu_{\text{H}_2}}$$

$$\frac{-0.5 \text{ mol}}{-1} = \frac{-0.5 \text{ mol}}{-1} = \frac{+0.5 \text{ mol}}{+1} = \frac{+1.5 \text{ mol}}{+3}$$



GO TO DIFFERENTIAL CHANGE ...

$$\frac{dn_{\text{CH}_4}}{\nu_{\text{CH}_4}} = \frac{dn_{\text{H}_2\text{O}}}{\nu_{\text{H}_2\text{O}}} = \frac{dn_{\text{CO}}}{\nu_{\text{CO}}} = \frac{dn_{\text{H}_2}}{\nu_{\text{H}_2}} \equiv d\xi$$

NEW TERM:

$$\boxed{\frac{dn_i}{\nu_i} \equiv d\epsilon}$$

WHERE ϵ IS THE REACTION COORDINATE
(AKA EXTENT)

REARRANGE:

$$\boxed{dn_i = \nu_i d\epsilon} \quad (i=1, 2, \dots, N)$$

INITIAL STATE ($t=0$)

$$\epsilon = 0 \quad + \quad n_i = n_{i0}$$

$$\int_{n_{i0}}^{n_i} dn_i = \nu_i \int_0^{\epsilon} d\epsilon$$

(6)

$$(n_i - n_{i0}) = \nu_i (\epsilon - 0)$$

$$\boxed{n_i = n_{i0} + \nu_i \epsilon} \quad (i=1, 2, \dots, N)$$

SUMMATION OVER ALL SPECIES

$$n = \sum_i n_i = \sum_i n_{i0} + \epsilon \sum_i \nu_i$$

total moles

REWRITE

$$\boxed{n = n_0 + \nu \epsilon}$$

WHERE:

$$n = \sum_i n_i$$

$$n_0 = \sum_i n_{i0}$$

$$\nu = \sum_i \nu_i$$

$$\boxed{y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \epsilon}{n_0 + \nu \epsilon}}$$

MOLE FRACTIONS

EXAMPLE 13.1 FOR A SYSTEM IN WHICH THE

FOLLOWING REACTION OCCURS,



ASSUME THERE ARE PRESENT INITIALLY 2 mol CH₄, 1 mol H₂O, 1 mol CO, and 4 mol H₂.

DETERMINE THE EXPRESSIONS FOR THE MOLE FRACTIONS y_i AS FUNCTIONS OF ϵ .

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \epsilon}{n_0 + \nu \epsilon}$$

<u>i</u>	<u>n_{i0}</u>	<u>ν_i</u>
CH ₄	2	-1
H ₂ O	1	-1
CO	1	+1
H ₂	4	+3
	<hr/> <u>$n_0 = 8$</u>	<hr/> <u>$\nu = 2$</u>

$$y_{\text{CH}_4} = \frac{2 - \epsilon}{8 + 2\epsilon}$$

$$y_{\text{H}_2\text{O}} = \frac{1 - \epsilon}{8 + 2\epsilon}$$

All functions
of a single
variable

$$y_{\text{CO}} = \frac{1 + \epsilon}{8 + 2\epsilon}$$

ϵ

$$y_{\text{H}_2} = \frac{4 + 3\epsilon}{8 + 2\epsilon}$$

Check $\sum_i y_i = 1$

$$\frac{(2 - \epsilon) + (1 - \epsilon) + (1 + \epsilon) + (4 + 3\epsilon)}{8 + 2\epsilon} = \frac{8 - 2\epsilon + 4\epsilon}{8 + 2\epsilon}$$

$$= 1 \quad \checkmark$$

MULTI REACTION STOICHIOMETRY

⇒ 2 OR MORE INDEPENDENT REACTIONS

Subscript j serves as the reaction index.

Then,

$$dn_i = \sum_j \nu_{i,j} dE_j \quad (i=1,2,\dots,N)$$

where E_j is extent of reaction j

$$n_i = n_{i0} + \sum_j \nu_{i,j} E_j$$

SUMMATION OVER ALL SPECIES:

$$n = \sum_i n_{i0} + \sum_i \sum_j \nu_{i,j} E_j = n_0 + \sum_j \left(\sum_i \nu_{i,j} \right) E_j$$

where $\nu_j = \sum_i \nu_{i,j} \Rightarrow$ $n = n_0 + \sum_j \nu_j E_j$

So, MOLE FRACTIONS ...

$$y_i = \frac{n_{i0} + \sum_j v_{i,j} \epsilon_j}{n_0 + \sum_j v_j \epsilon_j} \quad (i=1, 2, \dots, N)$$

EXAMPLE 13.3

CONSIDER A SYSTEM IN WHICH THE

FOLLOWING REACTIONS OCCUR:



WHERE THE NUMBERS (1) AND (2) INDICATE THE VALUE OF j , THE REACTION INDEX. IF THERE ARE PRESENT INITIALLY 2 mol CH_4 AND 3 mol H_2O , DETERMINE EXPRESSIONS FOR THE y_i AS FUNCTIONS OF ϵ_1 AND ϵ_2 .

$$n_{\text{CH}_4,0} = 2 \text{ mol}$$

$$n_{\text{H}_2\text{O},0} = 3 \text{ mol}$$

all others = 0

$$\Rightarrow n_0 = 2 + 3 + 0 = 5 \text{ mol}$$

Next, need $v_{i,j}$ and v_j .

$i =$	CH_4	H_2O	CO	CO_2	H_2	
$\frac{j}{}$						$\frac{v_j}{}$
1	-1	-1	+1	0	+3	2
2	-1	-2	0	+1	+4	2

$$y_{\text{CH}_4} = \frac{2 - \epsilon_1 - \epsilon_2}{5 + 2\epsilon_1 + 2\epsilon_2}$$

$$y_{\text{H}_2\text{O}} = \frac{3 - \epsilon_1 - 2\epsilon_2}{5 + 2\epsilon_1 + 2\epsilon_2}$$

$$y_{\text{CO}} = \frac{\epsilon_1}{5 + 2\epsilon_1 + 2\epsilon_2}$$

$$y_{\text{CO}_2} = \frac{\epsilon_2}{5 + 2\epsilon_1 + 2\epsilon_2}$$

$$y_{\text{H}_2} = \frac{3\epsilon_1 + 4\epsilon_2}{5 + 2\epsilon_1 + 2\epsilon_2}$$

All functions
of 2 variables:

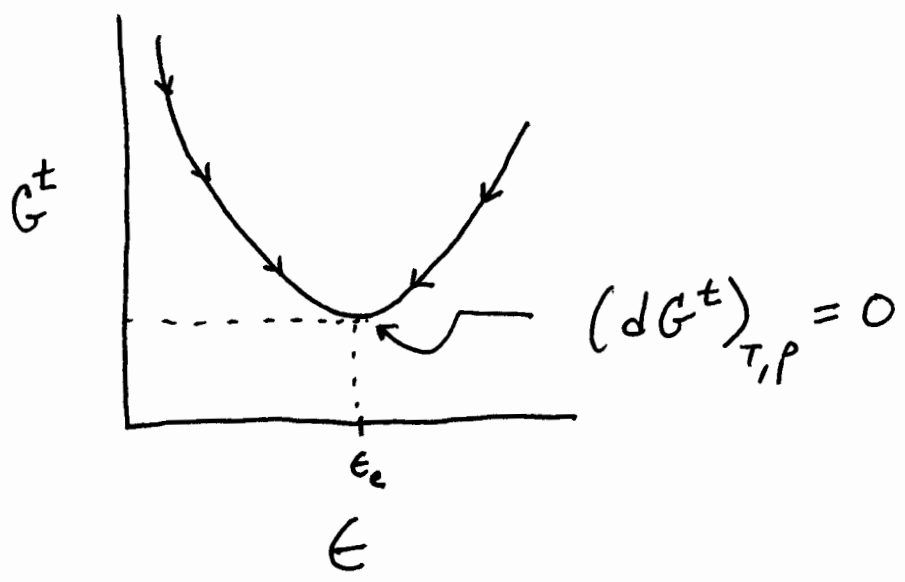
$$\epsilon_1 + \epsilon_2$$

13.2 Application of Equilibrium Criteria to Chemical Reactions.

@ EQUILIBRIUM $(dG^t)_{T,P} = 0$

If reaction occurs at constant T & P, then G^t must decrease.

GRAPHICALLY:



OR $\left(\frac{\partial G^t}{\partial \epsilon}\right)_{T,P} = 0$ (SLOPE)

AND G^t is minimized.

(NOTE: ONCE AGAIN SEE WHY GIBBS ENERGY IS SUCH AN IMPORTANT STATE FUNCTION)

13.3 RELATING STANDARD GIBBS ENERGY CHANGE AND EQUILIBRIUM CONSTANT.

RECALL:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$

BUT, FROM DEFINITION OF THE REACTION COORDINATE...

$$dn_i = \nu_i d\xi$$

SUBSTITUTE...

$$d(nG) = (nV)dP - (nS)dT + \sum_i \nu_i \mu_i d\epsilon$$

AT EQUILIBRIUM (constant T, P)

$$\left(\frac{\partial (nG)}{\partial \epsilon} \right)_{T, P} = 0 - 0 + \sum_i \nu_i \mu_i$$

⇒ CHEMICAL-REACTION EQUILIBRIUM CRITERIA

$$\sum_i \nu_i \mu_i = \left(\frac{\partial (nG)}{\partial \epsilon} \right)_{T, P} = 0$$

NOTE: μ_i CAN BE PUT IN TERMS OF G

AND

$$G = f(T, P, n_i)$$

... HOW TO GET THERE ... →

NEW TERM:

EQUILIBRIUM CONSTANT

$$K \equiv \exp\left(\frac{-\Delta G^\circ}{RT}\right)$$

OR

$$\ln K = -\frac{\Delta G^\circ}{RT}$$

where, $\Delta G^\circ = \sum_i \nu_i G_i^\circ$

and $G_i^\circ =$ Standard State Gibbs Energy at fixed pressure

$\Rightarrow f(T)$ only.

$\Rightarrow K = f(T)$ only.

$$\underline{\underline{K = f(T):}}$$

(16)

Recall, G is a Generating function for other state functions.

for example:

$$H_i^{\circ} = -RT^2 \frac{d(G_i^{\circ}/RT)}{dT}$$

and

$$\sum_i \nu_i H_i^{\circ} = -RT^2 \frac{d(\sum_i \nu_i G_i^{\circ}/RT)}{dT}$$

$$\Rightarrow \Delta H^{\circ} = -RT^2 \frac{d(\Delta G^{\circ}/RT)}{dT}$$

OR

$$\boxed{-\frac{\Delta H^{\circ}}{RT^2} = \frac{d(\Delta G^{\circ}/RT)}{dT}}$$

Recall:

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

$$\frac{d}{dT} (\ln K) = \frac{d}{dT} \left(-\frac{\Delta G^\circ}{RT} \right)$$

So

$$\frac{d(\ln K)}{dT} = + \frac{\Delta H^\circ}{RT^2}$$

Separate + Integrate:

$$d(\ln K) = \frac{\Delta H^\circ}{R} \frac{1}{T^2} dT$$

Limits:

$$T = T$$

$$K = K$$

$$T = T'$$

$$K = K'$$

$$\int_{K'}^K d(\ln K) = \frac{\Delta H^\circ}{R} \int_{T'}^T \frac{dT}{T^2}$$

$$\ln K \Big|_{K'}^K = \frac{\Delta H^\circ}{R} \left(\frac{-1}{T} \right) \Big|_{T'}^T$$

$$\ln \frac{K}{K'} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

Looks like a straight line. (see Fig. 13.2)

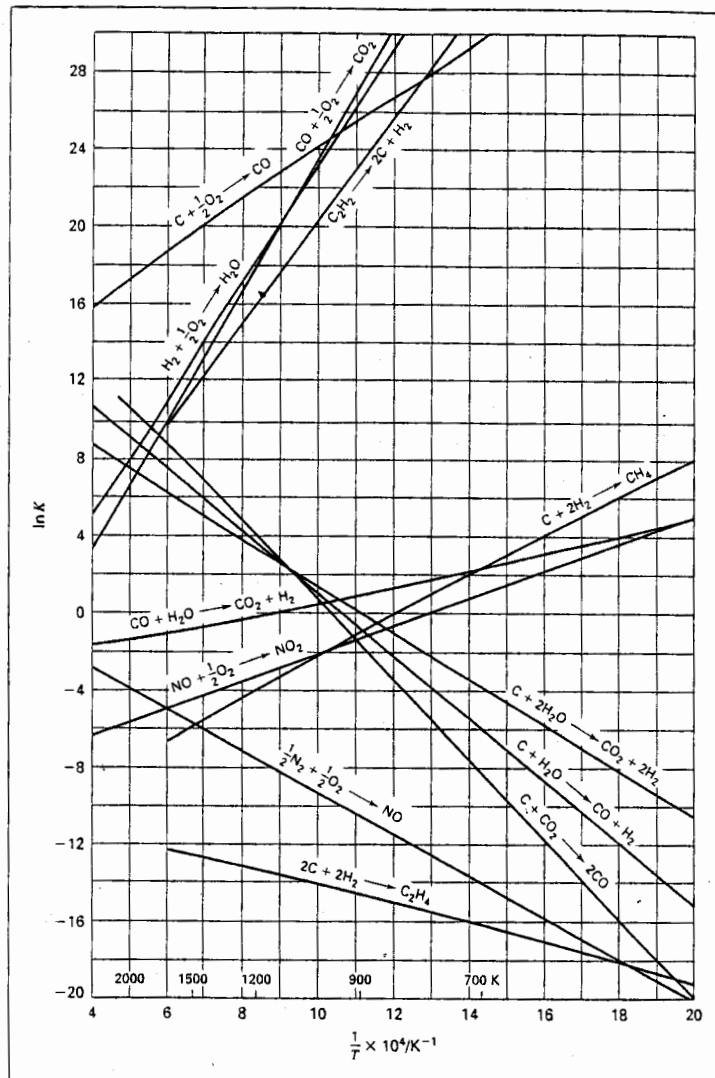


Figure 13.2: Equilibrium constants as a function of temperature.

How to GET K?

Need $\Delta G^\circ \leftarrow \Delta G$ @ reaction temperature.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

Recall from CHAP. 4

$$\Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT$$

Recall from CHAP. 5

$$\Delta S^\circ = \Delta S_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T}$$

where,
$$\Delta S_0^\circ = \frac{\Delta H_0^\circ - \Delta G_0^\circ}{T_0}$$

but, need a convenient T_0 .

Recall heats of formation.

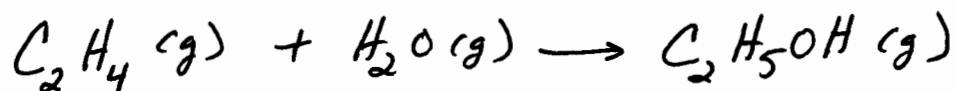
Standard values @ $T = 298\text{K}$.

Table C.4 (p. 686-687, Smith + Van Ness)

$$(\Delta H_{298}^{\circ} + \Delta G_{298}^{\circ})$$

\Rightarrow Convenient to use $T_0 = 298\text{K}$.

EXAMPLE 13.4 CALCULATE THE EQUILIBRIUM CONSTANT FOR THE VAPOR PHASE HYDRATION OF ETHYLENE AT 145°C AND 320°C FROM DATA GIVEN IN APPENDIX C.



TWO REACTION TEMPERATURES:

$$\left. \begin{array}{l} 145^{\circ}\text{C} \Rightarrow 418.15\text{K} \\ 320^{\circ}\text{C} \Rightarrow 593.15\text{K} \end{array} \right\} \text{Neither} = 298\text{K}$$

\Rightarrow Will need parameters for C_p .

<u>Species</u>	<u>A</u>	<u>$10^3 B$</u>	<u>$10^6 C$</u>	<u>$10^{-5} D$</u>
C_2H_4	1.424	14.394	-4.392	—
H_2O	3.470	1.450	—	0.121
C_2H_5OH	3.518	20.001	-6.002	—

Using reaction stoichiometry...

ΔA :

$$\Delta A = -1.424 - 3.470 + 3.518$$

$$\Delta A = -1.376$$

ΔB :

$$\Delta(10^3 B) = -14.394 - 1.450 + 20.001$$

$$\Delta B = 4.157 \times 10^{-3}$$

ΔC :

$$\Delta(10^6 C) = -(-4.392) + (-6.002)$$

$$\Delta C = -1.61 \times 10^{-6}$$

ΔD:

$$\Delta(10^{-5} D) = -0.121$$

$$\Delta D = -0.121 \times 10^5$$

NEXT, GET VALUES FOR STANDARD ENTHALPY + GIBBS ENERGY.

	<u>C₂H₄</u>	<u>H₂O</u>	<u>C₂H₅OH</u>
$\Delta H_{298,i}^{\circ}$	52,510	-241,818	-235,100
$\Delta G_{298,i}^{\circ}$	68,460	-228,572	-168,490

all in J/mol

$$\text{So, } \Delta H_{298}^{\circ} = \sum_i \nu_i \Delta H_{298,i}^{\circ}$$

$$= -52,510 - (-241,818) + (-235,100)$$

$$\Delta H_{298}^{\circ} = -45,792 \frac{\text{J}}{\text{mol}}$$

AND, $\Delta G_{298}^{\circ} = -68,460 - (-228,572) + (-168,490)$

$$\Delta G_{298}^{\circ} = -8,378 \frac{\text{J}}{\text{mol}}$$

$$\Delta S_{298}^{\circ} = \frac{-45,792 - (-8,378)}{298} = -125,55 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

Next, need values at the reaction temperature.

$$\Delta H^{\circ} = \Delta H_{298}^{\circ} + R \int_{298}^T \frac{\Delta C_p^{\circ}}{R} dT$$

ASIDE:

$$R \int_{298}^T \frac{\Delta C_p^{\circ}}{R} dT = R \int_{298}^T \left[-1.376 + 4.157 \times 10^{-3} T \right. \\ \left. - 1.61 \times 10^{-6} T^2 - \frac{0.121 \times 10^5}{T^2} \right] dT$$

$$= R \left\{ -1.376 T \Big|_{298}^T + \frac{4.157 \times 10^{-3}}{2} T^2 \Big|_{298}^T \right. \\ \left. - \frac{1.61 \times 10^{-6}}{3} T^3 \Big|_{298}^T + 0.121 \times 10^5 \frac{1}{T} \Big|_{298}^T \right\}$$

$$= R \left\{ -1.376(T-298) + \frac{4.157 \times 10^{-3}}{2} (T^2 - 298^2) - \frac{1.61 \times 10^{-6}}{3} (T^3 - 298^3) + 0.121 \times 10^5 \left(\frac{1}{T} - \frac{1}{298} \right) \right\}$$

Evaluate at each temperature:

$$\Delta H^\circ(418.15\text{K}) = -45,792 \frac{\text{J}}{\text{mol}} + R(-23.183\text{K})$$

$$= -45,792 \frac{\text{J}}{\text{mol}} + \frac{8.314 \text{ J}}{\text{mol}\cdot\text{K}} (-23.183\text{K})$$

$$\Delta H^\circ(418.15\text{K}) = -45,985 \frac{\text{J}}{\text{mol}}$$

$$\Delta H^\circ(593.15\text{K}) = -45,792 \frac{\text{J}}{\text{mol}} + \frac{8.314 \text{ J}}{\text{mol}\cdot\text{K}} (22.570\text{K})$$

$$\Delta H^\circ(593.15\text{K}) = -45,604 \frac{\text{J}}{\text{mol}}$$

Next, $\Delta S^\circ \dots$

$$\Delta S^\circ = \Delta S_{298}^\circ + R \int_{298}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T}$$

ASIDE:

$$R \int_{298}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = R \int_{298}^T \left[\frac{-1.376}{T} + 4.157 \times 10^{-3} \right.$$

$$\left. -1.61 \times 10^{-6} T - \frac{0.121 \times 10^5}{T^3} \right] dT$$

$$= R \left\{ -1.376 \ln T \Big|_{298}^T + 4.157 \times 10^{-3} T \Big|_{298}^T \right.$$

$$\left. - \frac{1.61 \times 10^{-6}}{2} T^2 \Big|_{298}^T + \frac{0.121 \times 10^5}{2} \frac{1}{T^2} \Big|_{298}^T \right\}$$

$$= R \left\{ -1.376 \ln \left(\frac{T}{298} \right) + 4.157 \times 10^{-3} (T - 298) \right.$$

$$\left. - \frac{1.61 \times 10^{-6}}{2} (T^2 - 298^2) + \frac{0.121 \times 10^5}{2} \left(\frac{1}{T^2} - \frac{1}{298^2} \right) \right\}$$

EVALUATE AT EACH TEMPERATURE:

$$\Delta S^\circ(418.15\text{K}) = \frac{-125.55\text{ J}}{\text{mol}\cdot\text{K}} + \frac{8.314\text{ J}}{\text{mol}\cdot\text{K}} (-0.0694)$$

$$\Delta S^\circ(418.15\text{K}) = \frac{-126.1\text{ J}}{\text{mol}\cdot\text{K}}$$

$$\Delta S^\circ(593.15\text{K}) = \frac{-125.55\text{ J}}{\text{mol}\cdot\text{K}} + \frac{8.314\text{ J}}{\text{mol}\cdot\text{K}} (0.0171)$$

$$\Delta S^\circ(593.15\text{K}) = \frac{-125.4\text{ J}}{\text{mol}\cdot\text{K}}$$

NEXT: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ(418.15\text{K}):$

$$= \frac{-45,985\text{ J}}{\text{mol}} - 418.15\text{ K} \left(\frac{-126.1\text{ J}}{\text{mol}\cdot\text{K}} \right)$$

$$\Delta G^\circ(418.15\text{K}) = \frac{6,743.7\text{ J}}{\text{mol}}$$

$$\underline{\Delta G^\circ (593.15 \text{ K}):}$$

$$= -45,604 \frac{\text{J}}{\text{mol}} - 593.15 \text{ K} \left(-\frac{125.4 \text{ J}}{\text{mol} \cdot \text{K}} \right)$$

$$\Delta G^\circ (593.15 \text{ K}) = 28,777.0 \frac{\text{J}}{\text{mol}}$$

FINALLY:

$$\ln K = -\frac{\Delta G^\circ}{RT}$$

$$K (418.15 \text{ K}) = \exp \left\{ \frac{-(6,743.7)}{(8.314)(418.15)} \right\} = 0.1437$$

$$K (593.15 \text{ K}) = \exp \left\{ \frac{-(28,777.0)}{(8.314)(593.15)} \right\} = 2.923 \times 10^{-3}$$

Next... Relating K to $x_i + y_i + \epsilon$

13.6 RELATION OF EQUILIBRIUM CONSTANTS TO COMPOSITION.

GAS PHASE REACTIONS

Starting Point:
$$\prod_i \left(\frac{\hat{f}_i}{f_i^\circ} \right)^{\nu_i} = K$$

where $f_i^\circ = P^\circ$ (Standard State Ideal Gas)

and
$$\hat{f}_i = \phi_i y_i P$$

fugacity

fugacity coefficient of
component "i" in solution

IF IDEAL SOLUTION

Then
$$\hat{\phi}_i = \phi_i$$

fugacity coefficient of pure
component "i"

SUBSTITUTE:

$$\prod_i \left(\frac{\phi_i y_i P}{P^0} \right)^{\nu_i} = K$$

FACTOR:

$$\prod_i \left(\frac{P}{P^0} \right)^{\nu_i} \prod_i (\phi_i y_i) = K$$

⏟

$$\left(\frac{P}{P^0} \right)^{\nu} \prod_i (\phi_i y_i) = K$$

$$\prod_i (\phi_i y_i) = \left(\frac{P}{P^0} \right)^{-\nu} K$$

HOWEVER, IF LOW PRESSURE \Rightarrow IDEAL GAS

$$\phi_i \rightarrow 1 \quad (\text{ideal gas})$$

$$\prod_i (y_i)^{\nu_i} = \left(\frac{P}{P^0}\right)^{-\nu} K$$

IDEAL
GAS
REACTION

↑
Composition
Term

↑
Pressure
Term

↑
Temperature
Term

AND CAN SOLVE FOR E_e , T , OR P IN TERMS OF THE OTHER TWO,

NOTES: 1) EFFECT OF TEMPERATURE ON K

a) ENDO THERMIC

$$\Delta H^0 \Rightarrow (+)$$

\Rightarrow AS $T \uparrow$, $K \uparrow$ and $\prod_i (y_i)^{\nu_i} \uparrow$

(AND $E_e \uparrow$)

b) EXOTHERMIC

$$\Delta H^\circ \rightarrow (-)$$

$$\Rightarrow \text{AS } T \uparrow, K \downarrow \text{ and } \prod_i (y_i)^{\nu_i} \downarrow$$

$$(\text{AND } E_e \downarrow)$$

2) Total Stoichiometric Number, ν

$$(\text{Recall, } \nu = \sum_i \nu_i)$$

a) for $\nu < 0$

$$\Rightarrow \text{AS } P \uparrow (\text{@ constant } T), \prod_i (y_i)^{\nu_i} \uparrow$$

$$(\text{AND } E_e \uparrow)$$

b) for $\nu > 0$

$$\Rightarrow \text{AS } P \uparrow (\text{@ constant } T), \prod_i (y_i)^{\nu_i} \downarrow$$

$$(\text{AND } E_e \downarrow)$$

LIQUID PHASE REACTIONS

Starting Point:
$$\prod_i \left(\frac{\hat{f}_i}{f_i^\circ} \right)^{\nu_i} = K$$

(just like for gas phase reactions)

where
$$\hat{f}_i = \gamma_i x_i f_i^\circ$$

$$\swarrow$$
 fugacity of pure liquid "i" @ Equilibrium T+P

So,

$$\frac{\hat{f}_i}{f_i^\circ} = \frac{\gamma_i x_i f_i^\circ}{f_i^\circ} = \gamma_i x_i \left(\frac{f_i}{f_i^\circ} \right)$$

But, liquid fugacities are weak functions of pressure, so...

$$\frac{f_i}{f_i^\circ} \approx 1 \quad \longrightarrow$$

$$\prod_i (x_i \gamma_i)^{\nu_i} = K$$

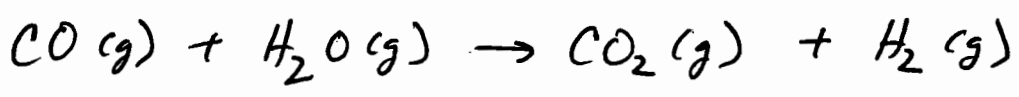
LOW TO
MODERATE
PRESSURE
LIQUID REACTIONS.

IF IDEAL SOLUTION, THEN $\gamma_i = 1$

$$\prod_i (x_i)^{\nu_i} = K$$

IDEAL LIQUIDS

EXAMPLE 13.5 THE WATER-GAS-SHIFT REACTION,



IS CARRIED OUT UNDER THE DIFFERENT SETS OF CONDITIONS DESCRIBED BELOW. CALCULATE THE FRACTION OF STEAM REACTED IN EACH CASE. ASSUME THE MIXTURE BEHAVES AS AN IDEAL GAS.

(a) The reactants consist of 1 mol of H_2O vapor and 1 mol of CO . The temperature is 1,100K and the pressure is 1 bar.

$$V=0 \Rightarrow \prod_i (y_i)^{\nu_i} = K$$

$$K = y_{\text{CO}}^{-1} y_{\text{H}_2\text{O}}^{-1} y_{\text{CO}_2}^{+1} y_{\text{H}_2}^{+1} = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}}$$

Next, using Figure 13.2 ...

$$T = 1,100 \text{ K} \Rightarrow \frac{1}{T} = 9.09 \times 10^{-4}$$

$$\text{and } \frac{1}{T} \times 10^4 = 9.09$$

$$\Rightarrow \ln K = 0 \Rightarrow K = 1$$

So,

$$\frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = 1$$

Next,
$$y_i = \frac{n_{i0} + \nu_i \epsilon}{n_0 + W \epsilon}$$

n_{i0} = initial moles component "i"

n_0 = initial total moles

$W = 0$

So,
$$y_{CO} = \frac{1 - \epsilon}{2}$$

$$y_{H_2O} = \frac{1 - \epsilon}{2}$$

$$y_{CO_2} = \frac{\epsilon}{2}$$

$$y_{H_2} = \frac{\epsilon}{2}$$

$\sum_i y_i = 1$ ✓

Plug & Chug:
$$K = \left(\frac{\epsilon}{2}\right)\left(\frac{\epsilon}{2}\right)\left(\frac{2}{1-\epsilon}\right)\left(\frac{2}{1-\epsilon}\right) = \frac{\epsilon^2}{(1-\epsilon)^2} = 1$$

Cross Multiply...

$$\epsilon^2 = (1-\epsilon)^2 = 1 - 2\epsilon + \epsilon^2$$

$$0 = 1 - 2\epsilon \Rightarrow \boxed{\epsilon = 0.5}$$

EQUILIBRIUM CONVERSION

FINALLY... ANSWER THE QUESTION

50% (or 0.5 fraction) of the steam reacts.

(f) Same conditions as (a) but with initial mixture 1 mol H_2O , 1 mol CO , and 1 mol CO_2 .

$$y_{\text{CO}} = \frac{1-\epsilon}{3}$$

$$y_{\text{CO}_2} = \frac{1+\epsilon}{3}$$

$$y_{\text{H}_2\text{O}} = \frac{1-\epsilon}{3}$$

$$y_{\text{H}_2} = \frac{\epsilon}{3}$$

$$K = 1 = \left(\frac{1+\epsilon}{3}\right)\left(\frac{\epsilon}{3}\right)\left(\frac{3}{1-\epsilon}\right)\left(\frac{3}{1-\epsilon}\right)$$

$$1 = \frac{(1+\epsilon)\epsilon}{(1-\epsilon)^2} \quad \text{Cross Multiply...}$$

$$1 - 2\epsilon + \epsilon^2 = \epsilon + \epsilon^2$$

$$1 = 3\epsilon \Rightarrow \boxed{\epsilon = 0.333}$$

\Rightarrow Fraction of steam reacted is 0.333.

(g) At 1,650 K, and same conditions as (a).

$$\frac{10^4}{T} = 6.06 \Rightarrow \ln K = -1 \quad (\text{from Fig. 13.2})$$

$$\Rightarrow \boxed{K = 0.368}$$

$$\frac{\epsilon^2}{(1-\epsilon)^2} = 0.368$$

$$2.717\epsilon^2 = 1 - 2\epsilon + \epsilon^2$$

(3)

$$1.717 \epsilon^2 + 2\epsilon - 1 = 0$$

Quadratic Formula:

$$\epsilon = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
$$= \frac{-2 \pm \sqrt{4 - 4(1.717)(-1)}}{2(1.717)}$$

So, $\epsilon = 0.378$ or -1.542

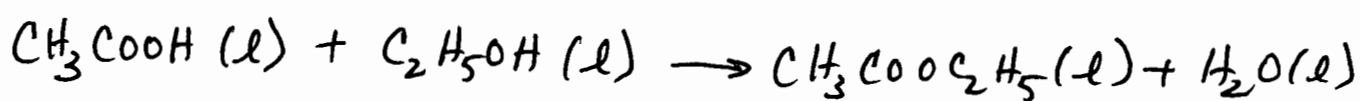
(but ϵ cannot be negative)

$\epsilon = 0.378$

Note: Exothermic reaction, so

$\epsilon \downarrow$ as $T \uparrow$,

EXAMPLE 13.8 ACETIC ACID IS ESTERIFIED IN THE LIQUID PHASE WITH ETHANOL AT 100°C AND ATMOSPHERIC PRESSURE TO PRODUCE ETHYL ACETATE AND WATER ACCORDING TO THE REACTION:



IF INITIALLY THERE IS ONE MOLE EACH OF ACETIC ACID AND ETHANOL, ESTIMATE THE MOLE FRACTION OF ETHYL ACETATE IN THE REACTING MIXTURE AT EQUILIBRIUM.

FIRST, CALCULATE ΔH_{298}° + ΔG_{298}°

Species	ΔH_{f298}°	ΔG_{f298}°
Ethanol	-277,690	-174,780
Acetic acid	-484,500	-389,900
Ethyl acetate	-480,000	-332,200
H ₂ O	-285,830	-237,129

$$\Delta H_{298}^{\circ} = -(-277,690) - (-484,500) \\ + (-480,000) + (-285,830)$$

$$\Delta H_{298}^{\circ} = -3,640 \text{ J}$$

$$\Delta G_{298}^{\circ} = -(-174,780) - (-389,900) \\ + (-332,200) + (-237,129)$$

$$\Delta G_{298}^{\circ} = -4,649 \text{ J}$$

So, @ 298K

$$\ln K_{298} = \frac{-\Delta G_{298}^{\circ}}{RT} = \frac{-(-4,649 \text{ J})}{\left(\frac{8.314 \text{ J}}{\text{mol}\cdot\text{K}}\right)(298 \text{ K})} = 1.876$$

$$\Rightarrow K_{298} = 6.5273$$

BUT, ACTUAL REACTION TEMPERATURE IS 373.15K

FOR SMALL TEMPERATURE CHANGES, APPROXIMATE
NEW K FROM:

$$\ln\left(\frac{K}{K'}\right) = -\frac{\Delta H^{\circ}}{R} \left(\frac{1}{T} - \frac{1}{T'}\right)$$

$$\ln\left(\frac{K}{6.5273}\right) = -\frac{(-3,640) \text{ J}}{\frac{8.314 \text{ J}}{\text{mol}\cdot\text{K}}} \left(\frac{1}{373.15} - \frac{1}{298}\right)$$

$$\ln\left(\frac{K}{6.5273}\right) = -0.2959$$

$$\Rightarrow K = 4.8554$$

Next,

$$X_{EtOH} = X_{AcAc} = \frac{1 - \epsilon}{2}$$

$$X_{EtAc} = X_{H_2O} = \frac{\epsilon}{2}$$

$$K = \left(\frac{\epsilon}{2}\right)\left(\frac{\epsilon}{2}\right)\left(\frac{2}{1-\epsilon}\right)\left(\frac{2}{1-\epsilon}\right) = \frac{\epsilon^2}{(1-\epsilon)^2}$$

But, $K = 4.8554$

$$4.8554 = \frac{\epsilon^2}{(1-\epsilon)^2}$$

$$1 - 2\epsilon + \epsilon^2 = 0.206\epsilon^2$$

$$1 - 2\epsilon + 0.794\epsilon^2 = 0$$

Quadratic Formula:

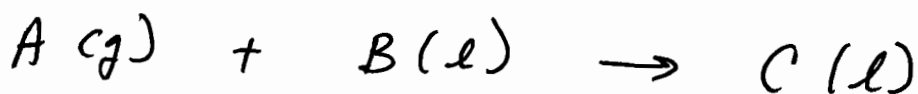
$$\epsilon = \frac{-(-2) \pm \sqrt{(-2)^2 - 4(0.794)(1)}}{(2)(0.794)}$$

$\epsilon = 1.831$ or 0.688

Finally, answer the question:

$$X_{\text{EtAc}} = \frac{0.688}{2} = 0.344$$

WHAT IF A HETEROGENEOUS SYSTEM?
(MIXED GAS/LIQUID)



$$K = \frac{\gamma_c x_c}{\left(\frac{\phi_A y_A P}{P^\circ}\right) (\gamma_B x_B)}$$

AND, IF IDEAL GAS/IDEAL LIQUID

$$K = \frac{x_c P^\circ}{(y_A P) x_B}$$

13.9 MULTI REACTION EQUILIBRIA

⇒ Extension of method for single reaction

$$\prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_{i,j}} = K_j$$

and

$$K_j \equiv \exp\left(\frac{-\Delta G_j^0}{RT}\right)$$

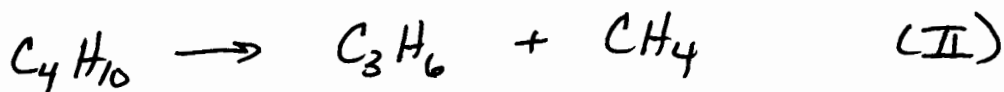
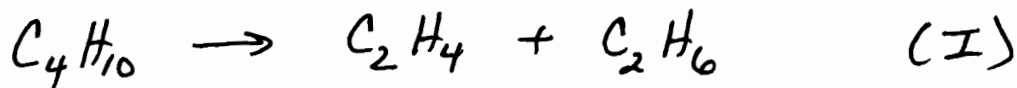
So, for gas phase reaction:

$$\prod_i \left(\frac{\hat{f}_i}{p^0} \right)^{\nu_{i,j}} = K_j$$

And, for ideal gas ...

$$\prod_i (y_i)^{\nu_{i,j}} = \left(\frac{P}{p^0} \right)^{-\nu_j} K_j$$

EXAMPLE 13.12 A FEED STOCK OF PURE n-BUTANE IS CRACKED AT 750K AND 1.2 BAR TO PRODUCE OLEFINS, ONLY TWO REACTIONS HAVE FAVORABLE EQUILIBRIUM CONVERSIONS AT THESE CONDITIONS:



IF THESE REACTIONS REACH EQUILIBRIUM, WHAT IS THE PRODUCT COMPOSITION? USING DATA FROM APP.C AND PROCEDURES IN EX. 13.4, THE EQUILIBRIUM CONSTANTS AT 750K ARE:

$$K_I = 3.856$$

$$K_{II} = 268.4$$

ALSO, WHICH PRODUCTS DO YOU EXPECT TO GENERATE IN HIGHER PROPORTION?

(HINT: LOOK AT K)

BASIS: 1 mol Butane (C_4H_{10}) Feed

$$\Rightarrow n_{C_4H_{10},0} = 1, \text{ all others} = 0$$

$$\Rightarrow n_0 = 1$$

$$V_I = \sum_i V_{i,I}$$

$$= -1 + 1 + 1$$

$$\boxed{V_I = 1}$$

$$V_{II} = \sum_i V_{i,II}$$

$$= -1 + 1 + 1$$

$$\boxed{V_{II} = 1}$$

So,

$$y_{C_4H_{10}} = \frac{1 - \epsilon_I - \epsilon_{II}}{1 + \epsilon_I + \epsilon_{II}}$$

$$y_{C_3H_4} = y_{C_2H_6} = \frac{\epsilon_I}{1 + \epsilon_I + \epsilon_{II}}$$

$$y_{C_3H_6} = y_{CH_4} = \frac{\epsilon_{II}}{1 + \epsilon_I + \epsilon_{II}}$$

Next,

$$K_I \left(\frac{P}{P_0} \right)^{-1} = \frac{y_{C_2H_4} y_{C_2H_6}}{y_{C_4H_{10}}} = \frac{\epsilon_I^2}{(1 - \epsilon_I - \epsilon_{II})(1 + \epsilon_I + \epsilon_{II})}$$

$$K_{II} \left(\frac{P}{P_0} \right)^{-1} = \frac{y_{C_3H_8} y_{CH_4}}{y_{C_4H_{10}}} = \frac{\epsilon_{II}^2}{(1 - \epsilon_I - \epsilon_{II})(1 + \epsilon_I + \epsilon_{II})}$$

TAKE RATIO:

$$\frac{K_{II}}{K_I} = \frac{\epsilon_{II}^2}{\epsilon_I^2} \Rightarrow \left(\frac{K_{II}}{K_I} \right)^{\frac{1}{2}} = \frac{\epsilon_{II}}{\epsilon_I}$$

$$\Rightarrow \epsilon_{II} = \epsilon_I \left(\frac{K_{II}}{K_I} \right)^{\frac{1}{2}}$$

If $k = \left(\frac{K_{II}}{K_I} \right)^{\frac{1}{2}}$, then

$$\boxed{\epsilon_{II} = k \epsilon_I}$$

SUBSTITUTE

$$K_I \left(\frac{P}{P^0} \right)^{-1} = \frac{\epsilon_I^2}{(1 - \epsilon_I - K\epsilon_I)(1 + \epsilon_I + K\epsilon_I)}$$

where $K_I = 3.856$

$$P = 1.2 \text{ bar}$$

$$P^0 = 1 \text{ bar (Standard Pressure)}$$

$$K = \left(\frac{268.4}{3.856} \right)^{1/2} = 8.343$$

Plug & Chug

$$(3.856) \left(\frac{1.2}{1} \right)^{-1} = \frac{\epsilon_I^2}{(1 - \epsilon_I - 8.343\epsilon_I)(1 + \epsilon_I + 8.343\epsilon_I)}$$

SOLVER:

$$\boxed{\epsilon_I = 0.1068}$$

$$\Rightarrow \epsilon_{II} = 8.343 \epsilon_I = \boxed{0.8910 = \epsilon_{II}}$$

S_o , product composition:

$$y_{C_4H_{10}} = \frac{1 - 0.1068 - 0.8910}{1 + 0.1068 + 0.8910}$$

$$y_{C_4H_{10}} = 0.0011$$

$$y_{C_2H_4} = y_{C_2H_6} = \frac{0.1068}{1 + 0.1068 + 0.8910}$$

$$y_{C_2H_4} = y_{C_2H_6} = 0.0534$$

$$y_{C_3H_8} = y_{CH_4} = \frac{0.8910}{1 + 0.1068 + 0.8910}$$

$$y_{C_3H_8} = y_{CH_4} = 0.4460$$

Check: $\sum_i y_i = 0.9999$ Pretty Close ✓
