

# KESETIMBANGAN REAKSI KIMIA

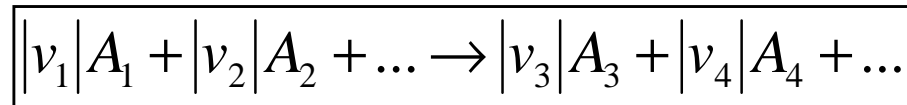
Dosen: Bregas S T Sembodo

# Reaksi Kimia

- Laju dan konversi kesetimbangan suatu reaksi kimia tergantung pada temperatur, tekanan, dan komposisi reaktan.
- **Laju reaksi** tidak rentan terhadap perlakuan termodinamika, **konversi kesetimbangan**, sebaliknya, rentan terhadap perlakuan termodinamika
- Tujuan dari kuliah ini adalah untuk mengetahui pengaruh suhu, tekanan, dan komposisi awal pada konversi kesetimbangan reaksi kimia.

# Koordinat Reaksi

- Reaksi Kimia secara umum:



$$\frac{dn_1}{v_1} = \frac{dn_2}{v_2} = \frac{dn_3}{v_3} = \frac{dn_4}{v_4} = \dots \equiv d\varepsilon$$

Koordinat reaksi, mencirikan tingkat atau derajat suatu reaksi telah berlangsung

- Perubahan diferensial dalam jumlah mol suatu spesies yg bereaksi :

$$dn_i = v_i d\varepsilon \quad (i = 1, 2, \dots, N)$$

$$\int_{n_{i0}}^{n_i} dn_i = v_i \int_0^\varepsilon d\varepsilon \quad (i = 1, 2, \dots, N)$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \varepsilon}{n_0 + v \varepsilon}$$

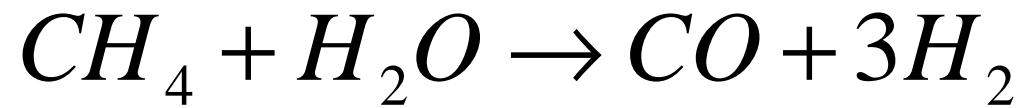
$$n = \sum_i n_i = n_0 + v \varepsilon$$

$$n_i = n_{i0} + v_i \varepsilon \quad (i = 1, 2, \dots, N)$$

Untuk sistem di mana reaksi berikut terjadi ,  $CH_4 + H_2O \rightarrow CO + 3H_2$   
Anggap mula-mula terdapat 2 mol  $CH_4$ , 1 mol  $H_2O$ , 1 mol  $CO$  and 4 mol  $H_2$ .  
Tentukan  $y_i$  sebagai fungsi  $\varepsilon$ .

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$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \varepsilon}{n_0 + v \varepsilon}$$



$$v = \sum_i v_i = -1 - 1 + 1 + 3 = 2$$

$$n_0 = \sum_i n_{i0} = 2 + 1 + 1 + 4 = 8$$

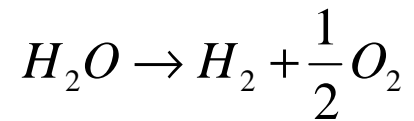
$$y_{CH_4} = \frac{2 - \varepsilon}{8 + 2\varepsilon}$$

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

$$y_{H_2O} = \frac{1 - \varepsilon}{8 + 2\varepsilon}$$

$$y_{H_2} = \frac{4 + 3\varepsilon}{8 + 2\varepsilon}$$

Suatu vesel awalnya berisi  $n_0$  mol uap air, jika dekomposisi terjadi menurut reaksi



tentukan hubungan jumlah mol dan fraksi mol masing-masing spesies kimia dengan koordinat reaksi  $\varepsilon$ .

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$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \varepsilon}{n_0 + v \varepsilon}$$

$$v = \sum_i v_i = -1 + 1 + \frac{1}{2} = \frac{1}{2}$$

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

$$y_{H_2O} = \frac{n_0 - \varepsilon}{n_0 + \frac{1}{2} \varepsilon}$$

$$n_{H_2O} = n_0 - \varepsilon$$

$$y_{O_2} = \frac{\frac{1}{2} \varepsilon}{n_0 + \frac{1}{2} \varepsilon}$$

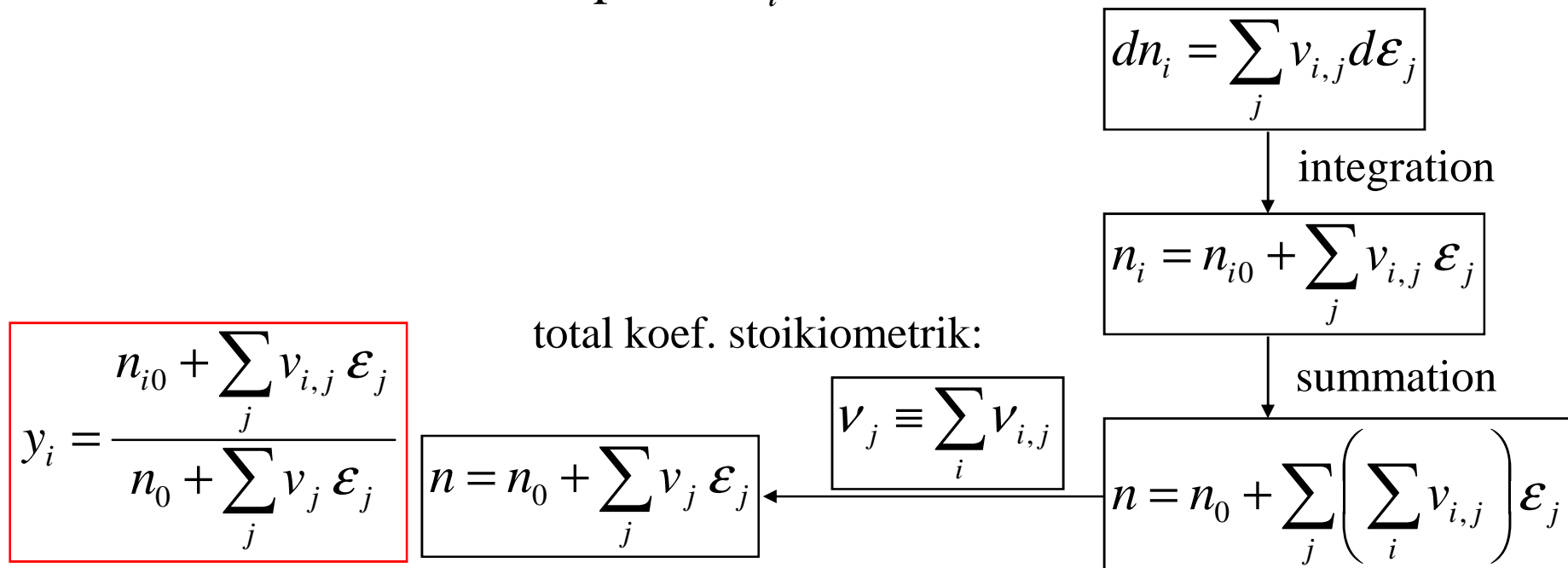
$$n_{O_2} = \frac{1}{2} \varepsilon$$

$$y_{H_2} = \frac{\varepsilon}{n_0 + \frac{1}{2} \varepsilon}$$

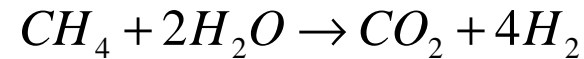
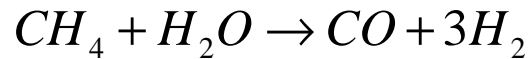
$$n_{H_2} = \varepsilon$$

# Multi reaksi

- Dua atau lebih reaksi berjalan simultan
  - $v_{i,j}$  : koefisien stoikiometrik spesies  $i$  dalam reaksi  $j$ .
  - Perubahan mol spesies  $n_i$ :



Consider a system in which the following reactions occur,



if there are present initially 2 mol  $CH_4$  and 3 mol  $H_2O$ , determine expressions for the  $y_i$  as functions of  $\varepsilon_1$  and  $\varepsilon_2$ .

$i$	$CH_4$	$H_2O$	$CO$	$CO_2$	$H_2$	
$j$						$v_j$
1	-1	-1	1	0	3	2
2	-1	-2	0	1	4	2

$$y_i = \frac{n_{i0} + \sum_j v_{i,j} \varepsilon_j}{n_0 + \sum_j v_j \varepsilon_j}$$

$$y_{CH_4} = \frac{2 - \varepsilon_1 - \varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{H_2O} = \frac{3 - \varepsilon_1 - 2\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{CO} = \frac{\varepsilon_1}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{CO_2} = \frac{\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{H_2} = \frac{3\varepsilon_1 + 4\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

# Aplikasi Kriteria Kesetimbangan pada Reaksi Kimia

- $\varepsilon$ : variabel tunggal yg menunjukkan perkembangan reaksi
  - Energi Gibbs total pada T dan P konstan ditentukan oleh  $\varepsilon$
  - Jika tidak dalam kesetimbangan, reaksi apapun akan mengalami penurunan Energi Gibbs total sistemnya
- Kondisi saat Kesetimbangan tercapai:
  - Energi Gibbs total adalah minimum  $G^t = f(\varepsilon) \rightarrow \min$
  - Differensial/ turunan pada titik itu sama dengan NOL

$$\left( dG^t \right)_{T,P} = 0$$



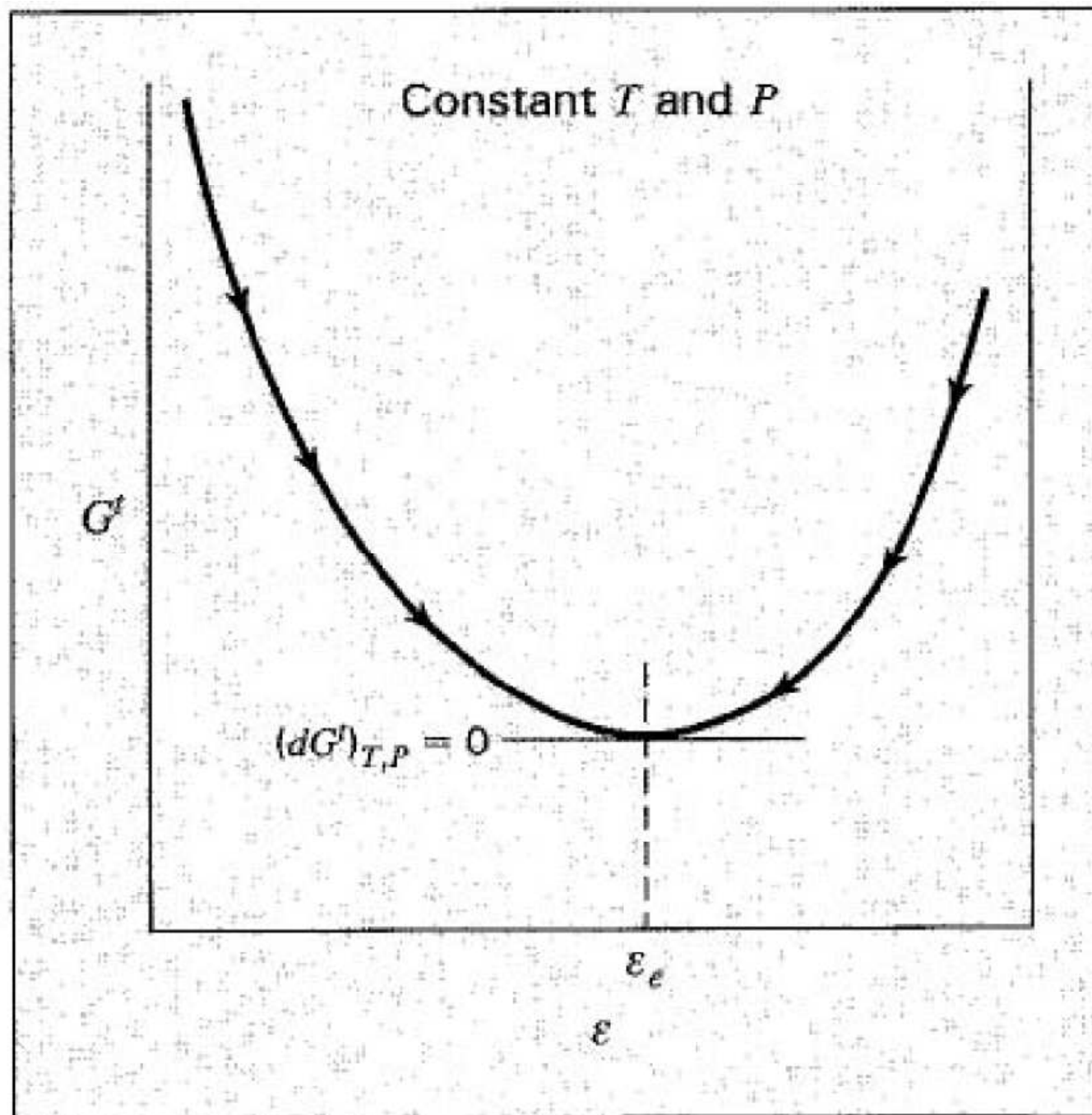


Figure 13.1 The total Gibbs energy in relation to the reaction coordinate

# Perubahan Energi Gibbs Standar dan Konstanta Kestimbangan

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

$$dn_i = \nu_i d\varepsilon$$

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

$$\sum_i \nu_i \mu_i = \left[ \frac{\partial(nG)}{\partial \varepsilon} \right]_{T,P} = \left[ \frac{\partial(G^t)}{\partial \varepsilon} \right]_{T,P} \xrightarrow{\text{at equilibrium}} = 0$$

The fugacity of a species in solution:

$$\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i$$

For pure species  $i$  in its standard state:

$$G_i^o = \Gamma_i(T) + RT \ln f_i^o$$

$$\prod_i \left( \frac{\hat{f}_i}{f_i^o} \right)^{\nu_i} = K$$

$$\mu_i - G_i^o = RT \ln \frac{\hat{f}_i}{f_i^o}$$

$$\sum_i \nu_i \mu_i = 0$$

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

$$\sum_i \nu_i \left( G_i^o + RT \ln \frac{\hat{f}_i}{f_i^o} \right) = 0$$

$$\Delta G^o \equiv \sum_i \nu_i G_i^o$$

$$\sum_i \nu_i G_i^o + RT \sum_i \left( \ln \frac{\hat{f}_i}{f_i^o} \right)^{\nu_i} = 0$$

$$\ln \prod_i \left( \frac{\hat{f}_i}{f_i^o} \right)^{\nu_i} = \frac{-\sum_i \nu_i G_i^o}{RT}$$

The equilibrium constant for the reaction, f(T)

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

The standard Gibbs energy change of reaction, f(T)

$$\Delta G^{\circ} \equiv \sum_i \nu_i G_i^{\circ}$$

Other standard property changes of reaction :

$$\Delta M^{\circ} \equiv \sum_i \nu_i M_i^{\circ}$$

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

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

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

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

For a chemical species in its standard state:

$$G_i^o = H_i^o - TS_i^o$$

summation

$$\sum_i \nu_i G_i^o = \sum_i \nu_i H_i^o - T \sum_i \nu_i S_i^o \rightarrow \Delta G^o = \Delta H^o - T \Delta S^o$$

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

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

$$\Delta S_0^o = \frac{\Delta H_0^o - \Delta G_0^o}{T_0}$$

$$\Delta G^o = \Delta H_0^o - \frac{T}{T_0} (\Delta H_0^o - \Delta G_0^o) + R \int_{T_0}^T \frac{\Delta C_P^o}{R} dT - RT \int_{T_0}^T \frac{\Delta C_P^o}{R} \frac{dT}{T}$$

$$\frac{\Delta G^\circ}{RT} = \frac{\Delta H_0^\circ}{RT} + \frac{(\Delta G_0^\circ - \Delta H_0^\circ)}{RT_0} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_P^\circ}{R} dT - \int_{T_0}^T \frac{\Delta C_P^\circ}{R} \frac{dT}{T}$$

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

Readily calculated at any temperature from the standard heat of reaction and the standard Gibbs energy change of reaction at a reference temperature

$$K = K_0 K_1 K_2$$

$$K_0 \equiv \exp\left(\frac{-\Delta G_0^\circ}{RT_0}\right)$$

$$K_1 \equiv \exp\left(\frac{\Delta H_0^\circ}{RT_0} \left(1 - \frac{T_0}{T}\right)\right)$$

$$K_2 \equiv \exp\left(-\frac{1}{T} \int_{T_0}^T \frac{\Delta C_P^\circ}{R} dT + \int_{T_0}^T \frac{\Delta C_P^\circ}{R} \frac{dT}{T}\right)$$

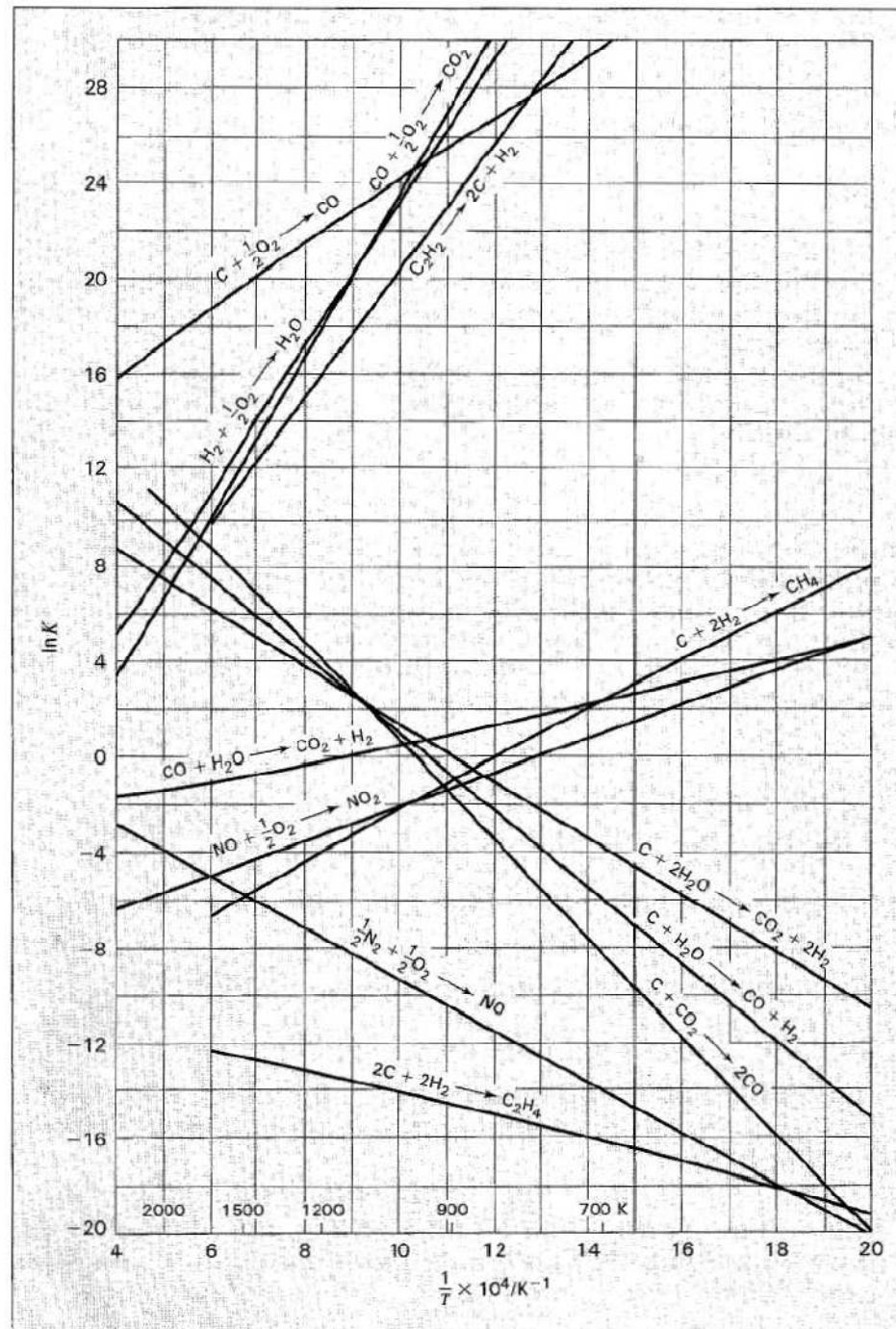
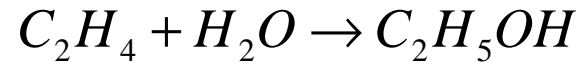


Figure 13.2 Equilibrium constants as a function of temperature

Calculation the equilibrium constant for the vapor-phase hydration of ethylene at 145 and at 320 °C from data given in App.c



$$K = K_0 K_1 K_2$$

$$K_0 \equiv \exp\left(\frac{-\Delta G_0^\circ}{RT_0}\right)$$

$$K_1 \equiv \exp\left(\frac{\Delta H_0^\circ}{RT_0} \left(1 - \frac{T_0}{T}\right)\right)$$

$$K_2 \equiv \exp\left(-\frac{1}{T} \int_{T_0}^T \frac{\Delta C_P^\circ}{R} dT + \int_{T_0}^T \frac{\Delta C_P^\circ}{R} \frac{dT}{T}\right)$$

From Table C.4

$$\Delta H_0^\circ = \Delta H_{298}^\circ = -45792 \text{ J/mol}$$

$$\Delta G_0^\circ = \Delta G_{298}^\circ = -8378 \text{ J/mol}$$

The heat capacity data:

$$\Delta = (C_2H_5OH) - (C_2H_4) - (H_2O)$$

T	K <sub>0</sub>	K <sub>1</sub>	K <sub>2</sub>	K
298.15	29.366	1	1	29.366
418.15	29.366	4.985x10 <sup>-3</sup>	0.986	1.443x10 <sup>-1</sup>
593.15	29.366	1.023x10 <sup>-4</sup>	0.9794	2.942x10 <sup>-3</sup>



- Reaksi fase Gas:

- Keadaan Gas Ideal:  $f_i^o = P^o$

- Standard-state pressure  $P^o$  of 1 bar

$$\prod_i \left( \frac{\hat{f}_i}{f_i^o} \right)^{\nu_i} = K \xrightarrow{f_i^o = P^o} \prod_i \left( \frac{\hat{f}_i}{P^o} \right)^{\nu_i} = K \xrightarrow{\begin{matrix} \hat{f}_i = \hat{\phi}_i y_i P \\ \nu \equiv \sum_i \nu_i \end{matrix}} \prod_i (y_i \hat{\phi}_i)^{\nu_i} = \left( \frac{P}{P^o} \right)^{-\nu} K$$

An ideal solution:  $\hat{\phi}_i = \phi_i$

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

An ideal gas:  $\phi_i = 1$

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

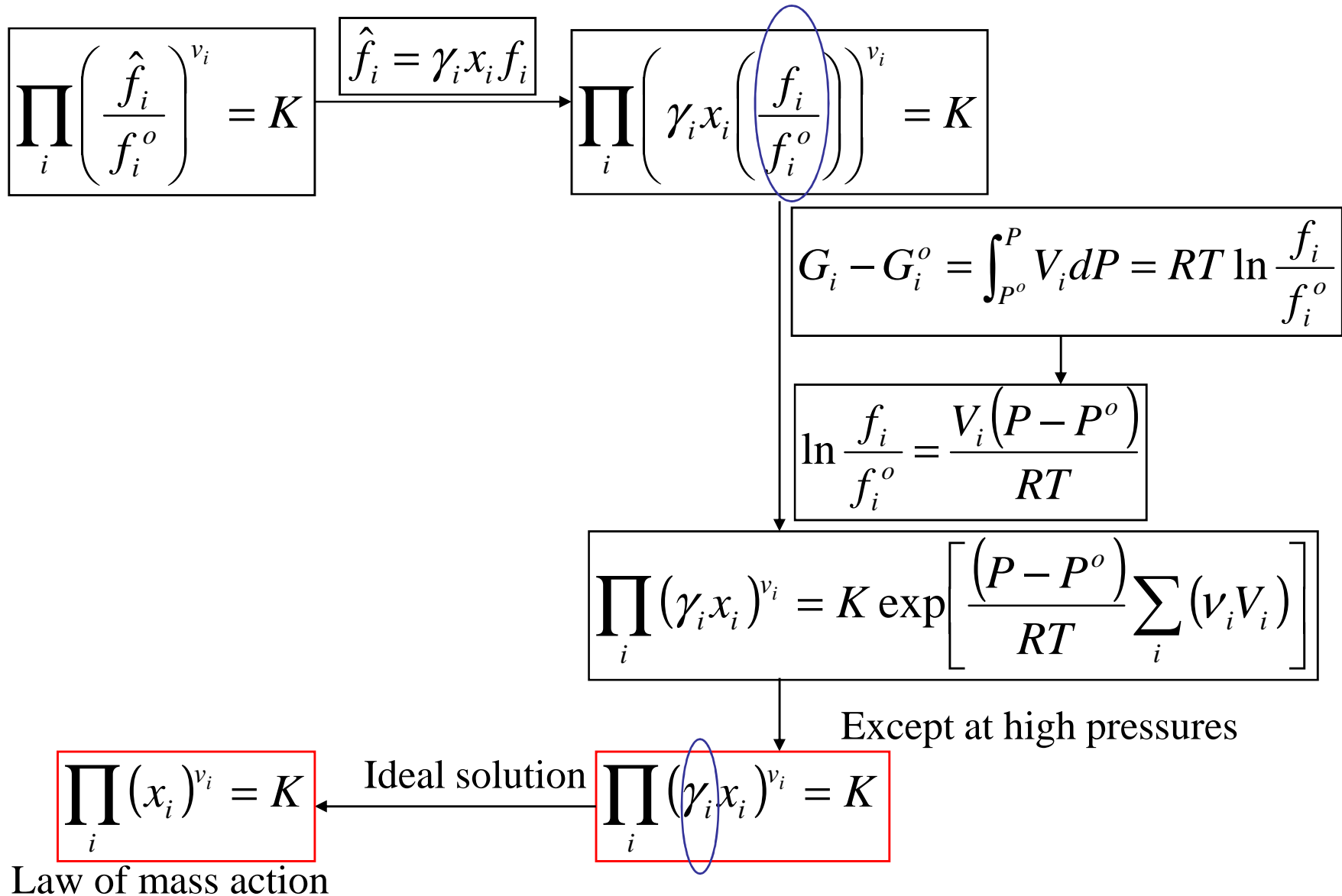
$f(\text{composition})$     $f(P)$     $f(T)$

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

$\downarrow$                        $\downarrow$                        $\downarrow$   
*f*(composition)    *f*(P)    *f*(T)

- According to Eq. (13.14), the effect of temperature on the equilibrium constant  $K$  is determined by the sign of  $\Delta H^\circ$ . Thus when  $\Delta H^\circ$  is positive, i.e., when the standard reaction is *endothermic*, an increase in  $T$  results in an increase in  $K$ . Equation (13.28) shows that an increase in  $K$  at constant  $P$  results in an increase in  $\prod_i (y_i)^{\nu_i}$ ; this implies a shift of the reaction to the right and an increase in  $\varepsilon_e$ . Conversely, when  $\Delta H^\circ$  is negative, i.e., when the standard reaction is *exothermic*, an increase in  $T$  causes a decrease in  $K$  and a decrease in  $\prod_i (y_i)^{\nu_i}$  at constant  $P$ . This implies a shift of the reaction to the left and a decrease in  $\varepsilon_e$ .
- If the total stoichiometric number  $\nu$  ( $\equiv \sum_i \nu_i$ ) is negative, Eq. (13.28) shows that an increase in  $P$  at constant  $T$  causes an increase in  $\prod_i (y_i)^{\nu_i}$ , implying a shift of the reaction to the right and an increase in  $\varepsilon_e$ . If  $\nu$  is positive, an increase in  $P$  at constant  $T$  causes a decrease in  $\prod_i (y_i)^{\nu_i}$ , a shift of the reaction to the left, and a decrease in  $\varepsilon_e$ .

- Liquid phase reaction:



# Equilibrium conversions for single reactions

- Single reaction in a homogeneous system:
  - assuming an ideal gas and the equilibrium constant is known:

known: 
$$\prod_i (y_i)^{v_i} = \left( \frac{P}{P^o} \right)^{-\nu} K$$

- assuming an ideal solution and the equilibrium constant is known:

known: 
$$\prod_i (x_i)^{v_i} = K$$

- the phase composition at equilibrium can be obtained

The water-gas-shift reaction,  $CO + H_2O \rightarrow CO_2 + H_2$  is carried out under the different sets of conditions described below. Calculate the fraction of steam reacted in each case. Assume the mixture behave as an ideal gas.

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$$\prod_i (y_i)^{v_i} = \left(\frac{P}{P^o}\right)^{-\nu} K \xrightarrow[\nu \equiv \sum_i v_i = 0]{\text{From Fig 13.2, } K = 1} \prod_i (y_i)^{v_i} = \frac{y_{H_2} y_{CO_2}}{y_{CO} y_{H_2O}} = 1$$

(a) the reactant consists of 1 mol of  $H_2O$  vapor and 1 mol of  $CO$ ,  $T = 1100$  K,  $P = 1$  bar

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \mathcal{E}}{n_0 + \nu \mathcal{E}} \rightarrow y_{CO} = \frac{1 - \mathcal{E}_e}{2} \quad y_{H_2O} = \frac{1 - \mathcal{E}_e}{2} \quad y_{CO_2} = \frac{\mathcal{E}_e}{2} \quad y_{H_2} = \frac{\mathcal{E}_e}{2} \quad \mathcal{E}_e = 0.5$$


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(b) the same as (a) except that the pressure is 10 bar

Since  $\nu = 0$ , the increase in pressure has no effect:  $\mathcal{E}_e = 0.5$

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(c) the same as (a) except that 2 mol of  $N_2$  is included in the reactants

Since  $N_2$  does not take part in the reaction and serves as a diluent:  $\mathcal{E}_e = 0.5$

(d) the reactants are 2 mol of H<sub>2</sub>O and 1 mol of CO. other conditions are the same as (a)

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \mathcal{E}}{n_0 + v \mathcal{E}} \rightarrow \begin{array}{|c|c|c|c|} \hline y_{CO} = \frac{1 - \mathcal{E}_e}{3} & y_{H_2O} = \frac{2 - \mathcal{E}_e}{3} & y_{CO_2} = \frac{\mathcal{E}_e}{3} & y_{H_2} = \frac{\mathcal{E}_e}{3} \\ \hline \end{array} \quad \mathcal{E}_e = 0.667$$

The fraction of steam that reacts is then  $0.667 / 2 = 0.333$

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(e) the reactants are 1 mol of H<sub>2</sub>O and 2 mol of CO. other conditions are the same as (a)

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \mathcal{E}}{n_0 + v \mathcal{E}} \rightarrow \begin{array}{|c|c|c|c|} \hline y_{CO} = \frac{2 - \mathcal{E}_e}{3} & y_{H_2O} = \frac{1 - \mathcal{E}_e}{3} & y_{CO_2} = \frac{\mathcal{E}_e}{3} & y_{H_2} = \frac{\mathcal{E}_e}{3} \\ \hline \end{array} \quad \mathcal{E}_e = 0.667$$

The fraction of steam that reacts is then 0.667

---

(f) the initial mixture consists of 1 mol of H<sub>2</sub>O, 1 mol of CO and 1 mol of CO<sub>2</sub>. other conditions are the same as (a)

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \mathcal{E}}{n_0 + v \mathcal{E}} \rightarrow \begin{array}{|c|c|c|c|} \hline y_{CO} = \frac{1 - \mathcal{E}_e}{3} & y_{H_2O} = \frac{1 - \mathcal{E}_e}{3} & y_{CO_2} = \frac{1 + \mathcal{E}_e}{3} & y_{H_2} = \frac{\mathcal{E}_e}{3} \\ \hline \end{array} \quad \mathcal{E}_e = 0.333$$

The fraction of steam that reacts is then 0.333

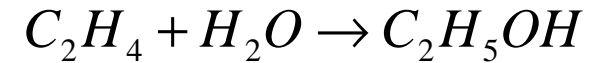
(g) same as (a) except that the temperature is 1650 K

$$\begin{array}{c}
 \boxed{\prod_i (y_i)^{v_i} = \left(\frac{P}{P^\circ}\right)^{-\nu} K} \xrightarrow[\boxed{\nu \equiv \sum_i v_i = 0}]{\text{From Fig 13.2, } K = 0.316} \boxed{\frac{y_{H_2} y_{CO_2}}{y_{CO} y_{H_2O}} = 0.316} \\
 \\
 \boxed{y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \mathcal{E}}{n_0 + \nu \mathcal{E}}} \rightarrow \boxed{y_{CO} = \frac{1 - \mathcal{E}_e}{2}} \boxed{y_{H_2O} = \frac{1 - \mathcal{E}_e}{2}} \boxed{y_{CO_2} = \frac{\mathcal{E}_e}{2}} \boxed{y_{H_2} = \frac{\mathcal{E}_e}{2}} \boxed{\mathcal{E}_e = 0.36}
 \end{array}$$

The reaction is exothermic, and conversion decreases with increasing temperature.

Estimate the maximum conversion of ethylene to ethanol by vapor phase hydration at 250°C and 35 bars for an initial steam-to-ethylene ratio of 5.

For a temperature of 250°C,  $K = 10.02 \times 10^{-3}$



Assuming the reaction mixture is an ideal solution.  $\hat{\phi}_i = \phi_i$   $v \equiv \sum_i \nu_i = -1$

$$\prod_i (y_i \hat{\phi}_i)^{\nu_i} = \left( \frac{P}{P^o} \right)^{-v} K \rightarrow \frac{y_{EtOH} \phi_{EtOH}}{y_{C_2H_4} \phi_{C_2H_4} y_{H_2O} \phi_{H_2O}} = \left( \frac{P}{P^o} \right) (10.02 \times 10^{-3})$$

	$T_c / K$	$P_c / \text{bar}$	$\omega$	$T_{ri}$	$P_{ri}$	$B^0$	$B^1$	$\phi_i$
$C_2H_4$	282.3	50.40	0.087	1.853	0.694	-0.074	0.126	0.977
$H_2O$	647.1	220.55	0.345	0.808	0.159	-0.511	-0.281	0.887
EtOH	513.9	61.48	0.645	1.018	0.569	-0.327	-0.021	0.827

$$\frac{y_{EtOH} \phi_{EtOH}}{y_{C_2H_4} \phi_{C_2H_4} y_{H_2O} \phi_{H_2O}} = \frac{y_{EtOH} (0.827)}{y_{C_2H_4} (0.977) y_{H_2O} (0.887)} = \left( \frac{35}{1} \right) (10.02 \times 10^{-3})$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \epsilon}{n_0 + \nu \epsilon} \quad y_{C_2H_4} = \frac{1 - \epsilon_e}{6 - \epsilon_e} \quad y_{H_2O} = \frac{5 - \epsilon_e}{6 - \epsilon_e} \quad y_{EtOH} = \frac{\epsilon_e}{6 - \epsilon_e} \quad \epsilon_e = 0.233$$



The equilibrium conversion is a function of temperature, pressure, and the steam-to-ethylene ratio in the feed:

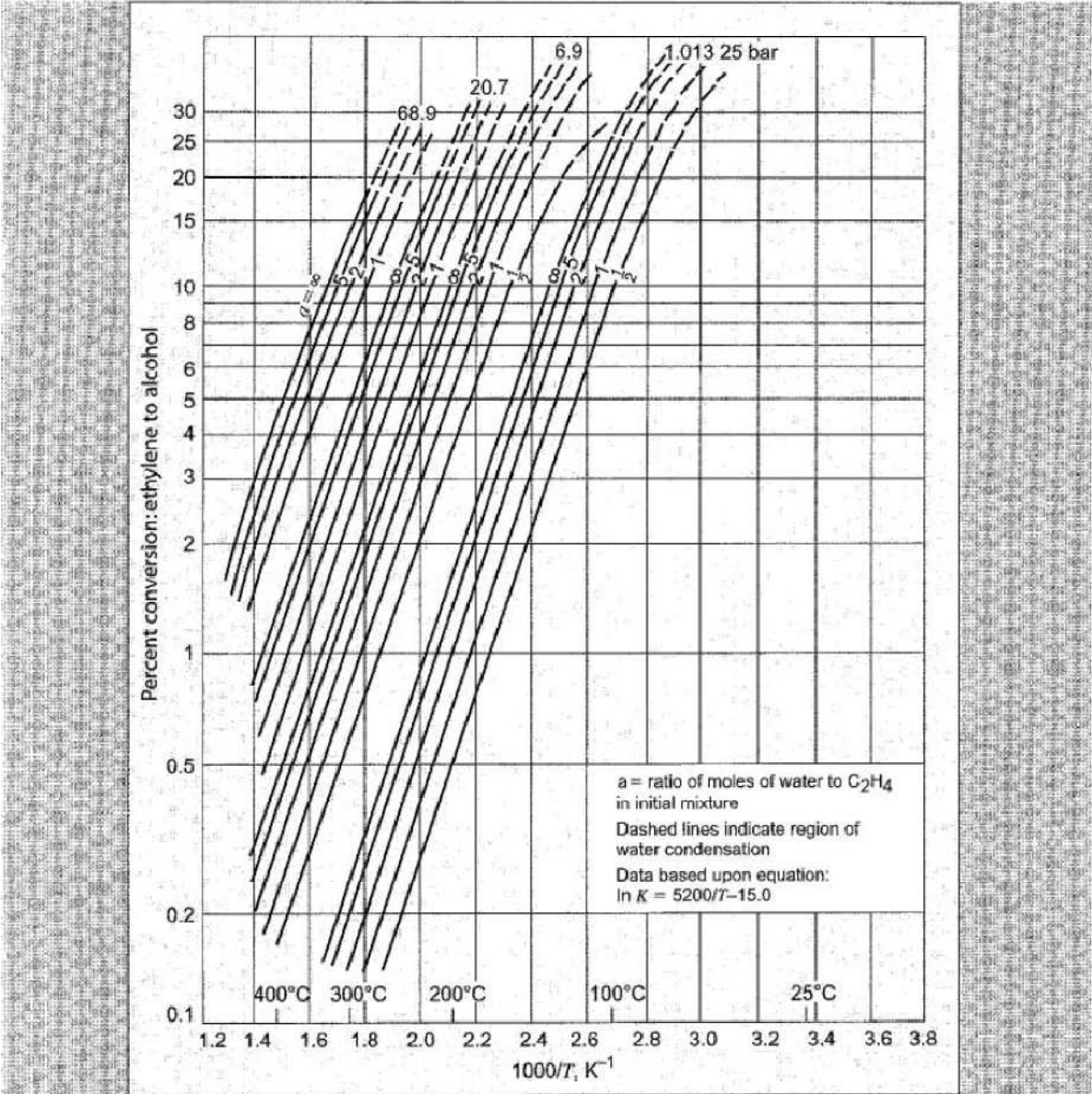
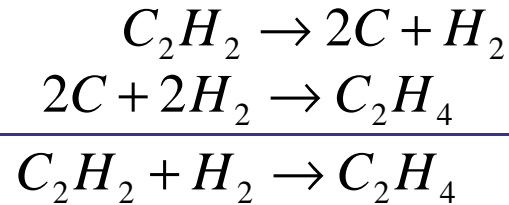


Figure 13.4 Equilibrium conversion of ethylene to ethyl alcohol in the vapor phase.

In a laboratory investigation, acetylene is catalytically hydrogenated to ethylene at 1120 °C and 1 bar. If the feed is an equimolar mixture of acetylene and hydrogen, what is the composition of the product stream at equilibrium?

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$$\Delta G^\circ = \Delta G_I^\circ + \Delta G_{II}^\circ$$

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

$$-RT \ln K = -RT \ln K_I - RT \ln K_{II}$$

$$K = K_I K_{II} = (4 \times 10^5)(2.5 \times 10^{-6}) = 1$$

$$\prod_i (y_i)^{v_i} = \left( \frac{P}{P^\circ} \right)^{-v} K$$

Ideal gas

$$\frac{y_{C_2H_4}}{y_{H_2} y_{C_2H_2}} = 1$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \epsilon}{n_0 + v \epsilon}$$

$$y_{H_2} = \frac{1 - \epsilon_e}{2 - \epsilon_e}$$

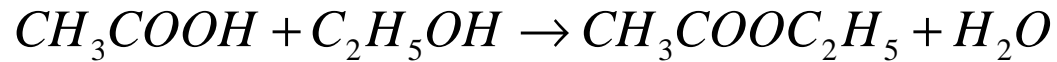
$$y_{C_2H_2} = \frac{1 - \epsilon_e}{2 - \epsilon_e}$$

$$y_{C_2H_4} = \frac{\epsilon_e}{2 - \epsilon_e}$$

$$\epsilon_e = 0.293$$

$$y_{C_2H_4} = 0.172 \quad y_{H_2} = y_{C_2H_2} = 0.414$$

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 1 mol of each of acetic acid and ethanol, estimate the mole fraction of ethyl acetate in the reacting mixture at equilibrium.

---

For the reaction at standard state (298 K):

$$\begin{array}{l} \Delta H_{298}^\circ = -3640 \text{ J} \\ \Delta G_{298}^\circ = -4650 \text{ J} \end{array} \xrightarrow{\ln K = \frac{-\Delta G^\circ}{RT}} \ln K = \frac{-\Delta G_{298}^\circ}{RT} = \frac{4650}{8.314 \times 298.15} = 1.8759 \xrightarrow{\frac{\Delta H^\circ}{RT^2} = \frac{d \ln K}{dT}} K_{373} = 4.8586$$

Assuming ideal solution:

$$\prod_i (x_i)^{v_i} = K \rightarrow \frac{x_{\text{EtAc}} x_{\text{H}_2\text{O}}}{x_{\text{AcH}} x_{\text{EtOH}}} = K$$

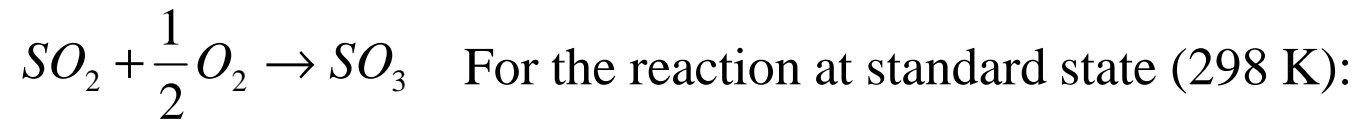
$$x_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \epsilon}{n_0 + v \epsilon}$$

$$x_{\text{AcH}} = x_{\text{EtOH}} = \frac{1 - \epsilon_e}{2} \quad x_{\text{EtAc}} = x_{\text{H}_2\text{O}} = \frac{\epsilon_e}{2}$$

$$\epsilon_e = 0.6879$$

$$x_{\text{EtAc}} = 0.6879 / 2 = 0.344$$

The gas phase oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  is carried out at a pressure of 1 bar with 20% excess air in an adiabatic reactor. Assuming that the reactants enter at  $25^\circ\text{C}$  and that equilibrium is attained at the exit, determine the composition and temperature of the product stream from the reactor



$$\Delta H_{298}^{\circ} = -98890 \text{ J}$$

$$\Delta G_{298}^{\circ} = -70866 \text{ J}$$

Assuming 1 mol of  $\text{SO}_2$  entering the reactor,

$\text{O}_2$ :  $0.5 \times (1.2) = 0.6$  mol entering

$\text{N}_2$ :  $0.6 \times (79/12) = 2.257$  mol entering

In the product stream:

$\text{SO}_2$ : $1 - \varepsilon_e$	$\text{SO}_3$ : $\varepsilon_e$
$\text{O}_2$ : $0.6 - 0.5\varepsilon_e$	$\text{N}_2$ : 2.257

→ total moles:  $3.857 - 0.5\varepsilon_e$

Energy balance:

$$\Delta H_{298}^{\circ} \varepsilon_e + \Delta H_P^{\circ} = \Delta H = 0$$

$$T = \frac{-\Delta H_{298}^{\circ} \varepsilon_e}{\langle C_P^{\circ} \rangle_H} + 298.15$$

The enthalpy change of the products at T

$$\Delta H_P^{\circ} = \langle C_P^{\circ} \rangle_H (T - 298.15) = \sum_i n_i \langle C_{Pi}^{\circ} \rangle_H (T - 298.15)$$

Assuming ideal gas:

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

$$\nu \equiv \sum_i \nu_i = 0.5$$

$$\left( \frac{\varepsilon_e}{1 - \varepsilon_e} \right) \left( \frac{3.857 - 0.5\varepsilon_e}{0.6 - 0.5\varepsilon_e} \right)^{0.5} = K$$

$$K = K_0 K_1 K_2$$

$$K_0 \equiv \exp\left( \frac{-\Delta G_0^o}{RT_0} \right)$$

$$K_1 \equiv \exp\left( \frac{\Delta H_0^o}{RT_0} \left( 1 - \frac{T_0}{T} \right) \right)$$

$$K_2 \equiv \exp\left( -\frac{1}{T} \int_{T_0}^T \frac{\Delta C_P^o}{R} dT + \int_{T_0}^T \frac{\Delta C_P^o}{R} \frac{dT}{T} \right)$$

$$\ln K = -11.3054 + \frac{11894.4}{T} + IDCPS - \frac{1}{T} (IDCPH)$$

Assume T → ln K → ε<sub>e</sub> → T



Converges at T = 855.7 K, ε<sub>e</sub> = 0.77

$$y_{SO_2} = \frac{1 - \varepsilon_e}{3.857 - 0.5 \times \varepsilon_e} = 0.0062$$

...

- Reactions in heterogeneous systems
  - a criterion of vapor/liquid equilibrium, must be satisfied along with the equation of chemical-reaction equilibrium

Estimate the compositions of the liquid and vapor phases when ethylene reacts with water to form ethanol at 200°C and 34.5 bar, conditions which assure the presence of both liquid and vapor phases. The reaction vessel is maintained at 34.5 bar by connection to a source of ethylene at this pressure. Assume no other reactions.

According to phase rule (see later):  $F = 2$  (say, P, T)  
 the material balance equations do not enter into the solution of this problem.

Regarding the reaction occurring in the vapor phase:  $C_2H_{2(g)} + H_2O_{(g)} \rightarrow C_2H_5OH_{(g)}$

Assuming ideal gas :

$$\prod_i \left( \frac{\hat{f}_i}{P^o} \right)^{v_i} = K \longrightarrow K = \frac{\hat{f}_{EtOH}}{\hat{f}_{C_2H_4} \hat{f}_{H_2O}} P^o \begin{matrix} P^o = 1 \text{ bar} \\ T = 473.15 \text{ K} \end{matrix} \longrightarrow K_{473.15 \text{ K}} = 0.031$$

$$K = \frac{\hat{f}_{EtOH}}{\hat{f}_{C_2H_4} \hat{f}_{H_2O}} P^o$$

Phase equilibrium:

$$\hat{f}_i^v = \hat{f}_i^l$$

$$K = \frac{\hat{f}_{EtOH}^v}{\hat{f}_{C_2H_4}^v \hat{f}_{H_2O}^v} P^o = \frac{\hat{f}_{EtOH}^l}{\hat{f}_{C_2H_4}^l \hat{f}_{H_2O}^l} P^o$$

For vapor phase:  $\hat{f}_i^v = y_i \hat{\phi}_i P$

For liquid phase:  $\hat{f}_i^l = x_i \gamma_i f_i^l$

$$K = \frac{x_{EtOH} \gamma_{EtOH} f_{EtOH}^l}{\left( y_{C_2H_4} \hat{\phi}_{C_2H_4} P \right) \left( x_{H_2O} \gamma_{H_2O} f_{H_2O}^l \right)} P^o$$

$$f_i^l \sim f_i^{sat} = \phi_i^{sat} P_i^{sat}$$

Ideal solution (vapor):  $\phi_i = \hat{\phi}_i$

$$K = \frac{x_{EtOH} \gamma_{EtOH} \phi_{EtOH}^{sat} P_{EtOH}^{sat}}{\left( y_{C_2H_4} \phi_{C_2H_4} P \right) \left( x_{H_2O} \gamma_{H_2O} \phi_{H_2O}^{sat} P_{H_2O}^{sat} \right)} P^o$$

$$K = \frac{x_{EtOH} \gamma_{EtOH} \phi_{EtOH}^{sat} P_{EtOH}^{sat}}{(y_{C_2H_4} \phi_{C_2H_4} P)(x_{H_2O} \gamma_{H_2O} \phi_{H_2O}^{sat} P_{H_2O}^{sat})} P^o$$

Known values:

$$P, T, \phi_{H_2O}^{sat}, \phi_{EtOH}^{sat}, \phi_{C_2H_4}, P_{H_2O}^{sat}, P_{EtOH}^{sat}$$

$$K = \frac{0.0493 x_{EtOH} \gamma_{EtOH}}{(y_{C_2H_4})(x_{H_2O} \gamma_{H_2O})}$$

$$y_{C_2H_4} = 1 - y_{EtOH} - y_{H_2O}$$

$$y_i = \frac{x_i \gamma_i \phi_i^{sat} P_i^{sat}}{\phi_i P}$$

$$y_{C_2H_4} = 1 - \frac{x_{EtOH} \gamma_{EtOH} \phi_{EtOH}^{sat} P_{EtOH}^{sat}}{\phi_{EtOH} P} - \frac{x_{H_2O} \gamma_{H_2O} \phi_{H_2O}^{sat} P_{H_2O}^{sat}}{\phi_{H_2O} P}$$

$$y_{C_2H_4} = 1 - 0.907 x_{EtOH} \gamma_{EtOH} - 0.493 x_{H_2O} \gamma_{H_2O}$$

$$x_{H_2O} = 1 - x_{EtOH} - x_{C_2H_4}$$

volatile



$$K = \frac{0.0493 x_{EtOH} \gamma_{EtOH}}{(y_{C_2H_4})(x_{H_2O} \gamma_{H_2O})}$$

$$y_{C_2H_4} = 1 - 0.907 x_{EtOH} \gamma_{EtOH} - 0.493 x_{H_2O} \gamma_{H_2O}$$

$$x_{H_2O} = 1 - x_{EtOH}$$

Values of  $\gamma_{EtOH}$ ,  $\gamma_{H_2O}$  are determined experimentally

Assume  $x_{EtOH} \rightarrow x_{H_2O} \rightarrow y_{C_2H_4} \rightarrow K$

check  $K_{473.15K} = 0.031$

Converged at:

	$x_i$	$y_i$
EtOH	0.06	0.180
H <sub>2</sub> O	0.94	0.464
C <sub>2</sub> H <sub>4</sub>	0.00	0.356
	$\Sigma = 1$	$\Sigma = 1$

# Phase rule and Duhem's theorem for reacting systems

- For non-reacting systems
  - $\pi$  phases and  $N$  chemical species:
- For reacting systems
  - Phase rule variables in each phase: temperature, pressure and  $N-1$  mole fraction. Total number of these variable:  $2 + (N-1) \pi$
  - Phase-equilibrium equations:  $(\pi-1) N$
  - $r$  independent chemical reactions at equilibrium within the system:  $r$  equations
  - $F = [2+(N-1) \pi ] - [(\pi-1) N] - [r] :$
  - With special constraints  $s$ :

$$F = 2 - \pi + N$$

$$F = 2 - \pi + N - r$$

$$F = 2 - \pi + N - r - s$$

Determine the number of degree of freedom  $F$  for each of the following systems:

- (a) A system of two miscible non-reacting species which exists as an azeotrope in vapor/liquid equilibrium.
  - (b) A system prepared by partially decomposing  $\text{CaCO}_3$  into an evacuated space.
  - (c) A system prepared by partially decomposing  $\text{NH}_4\text{Cl}$  into an evacuated space.
  - (d) A system consisting of the gases  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_4$  in chemical equilibrium
- 

- (a) Two non-reacting species in two phases

With no azeotrope:  $F = 2 - \pi + N - r = 2 - 2 + 2 - 0 = 2$

With azeotrope ( $x_1=y_1$ , one constraint):  $F = 2 - \pi + N - r - s = 1$

- (b) Single reaction:  $\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$

Three chemical species and three phases:  $\text{CaCO}_{3(s)}$   $\text{CaO}_{(s)}$   $\text{CO}_{2(g)}$

$F = 2 - \pi + N - r = 2 - 3 + 3 - 1 = 1$

- (c) Single reaction:  $\text{NH}_4\text{Cl}_{(s)} \rightarrow \text{NH}_{3(g)} + \text{HCl}_{(g)}$

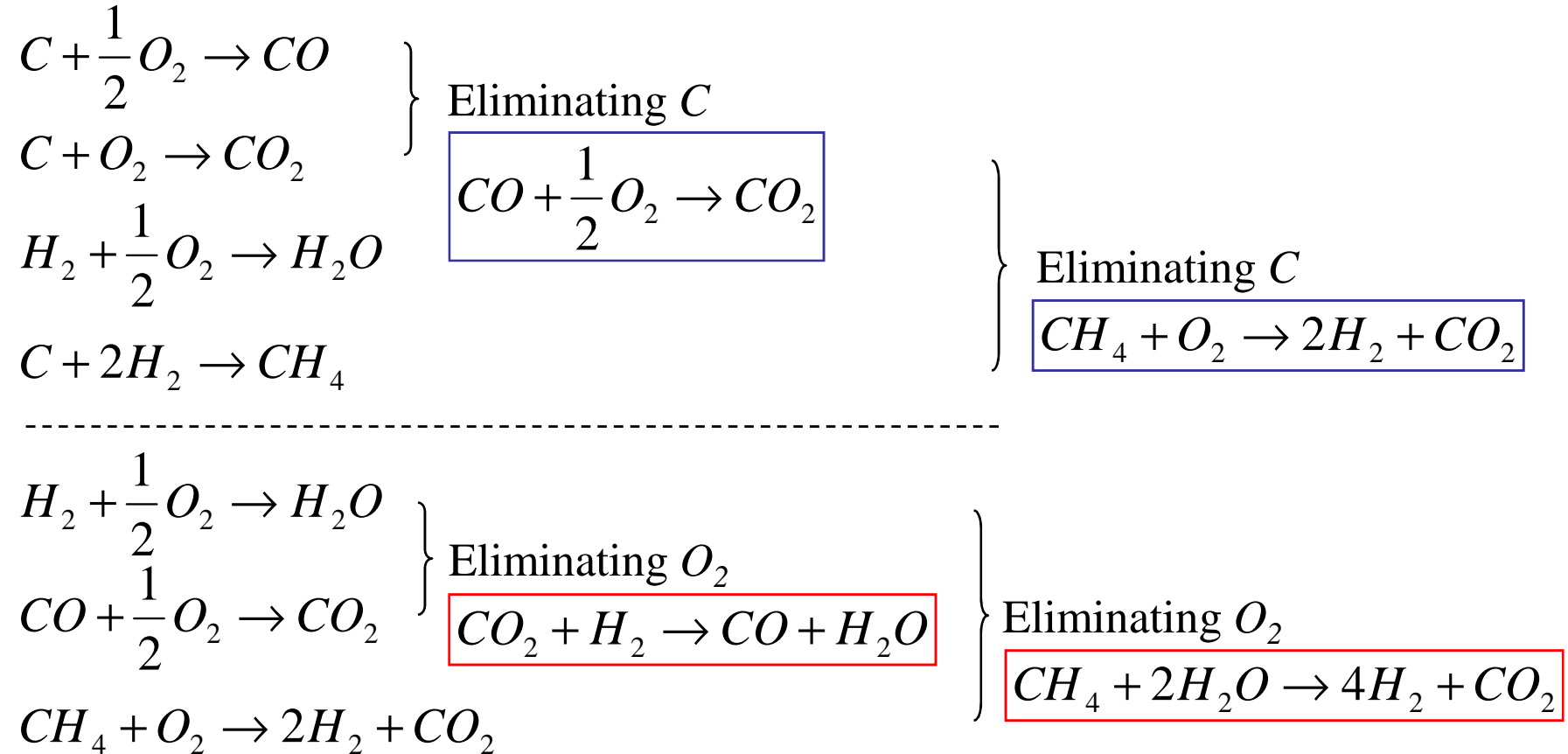
Three chemical species and two phases:  $\text{NH}_4\text{Cl}_{(s)}$   $\text{NH}_{3(g)} + \text{HCl}_{(g)}$

One constraint: gas phase is equimolar

$F = 2 - \pi + N - r - s = 2 - 2 + 3 - 1 - 1 = 1$

(d) 5 species, a single gas phase, and no special constraints:  $F = 2 - \pi + N - \underbrace{r}_{???} - s$

The formation reactions:



$$r = 2$$

$$\boxed{F = 2 - \pi + N - r - s = 2 - 1 + 5 - 2 - 0 = 4}$$

# Duhem's theorem

- For non-reacting system :
  - For any closed system formed initially from given masses of particular chemical species, the equilibrium state is completely determined by specification of any two independent variables.
  - $F = [2 + (N - 1)\pi + \pi] - [(\pi - 1)N + N] = 2$
- For reacting system:
  - A variable is introduced for each independent reaction:  $\varepsilon_j$
  - A equilibrium relation can be written for each independent reaction
  - $F = [2 + (N - 1)\pi + \pi] - [(\pi - 1)N + N] + 1 - 1 = 2$

# Multireaction equilibria

- A separate equilibrium constant is evaluated for each reaction:

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

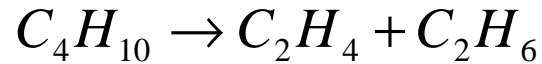
– gas phase reaction

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

Ideal gas

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

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?

---

Assuming ideal gas:

$$\prod_i (y_i)^{v_{i,j}} = \left( \frac{P}{P^o} \right)^{-v_j} K_j \rightarrow \begin{cases} \frac{y_{C_2H_4} y_{C_2H_6}}{y_{C_4H_{10}}} = \left( \frac{P}{P^o} \right)^{-1} K_I \\ \frac{y_{C_3H_6} y_{CH_4}}{y_{C_4H_{10}}} = \left( \frac{P}{P^o} \right)^{-1} K_{II} \end{cases}$$

With a basis of 1 mol of n-butane feed:

$$\begin{aligned} y_{C_4H_{10}} &= \frac{1 - \varepsilon_I - \varepsilon_{II}}{1 + \varepsilon_I + \varepsilon_{II}} & y_{C_2H_4} = y_{C_2H_6} &= \frac{\varepsilon_I}{1 + \varepsilon_I + \varepsilon_{II}} & y_{C_3H_6} = y_{CH_4} &= \frac{\varepsilon_{II}}{1 + \varepsilon_I + \varepsilon_{II}} \end{aligned}$$

$$\varepsilon_I = 0.1068 \quad \varepsilon_{II} = 0.8914 \quad y_{C_4H_{10}} = 0.001 \quad y_{C_2H_4} = y_{C_2H_6} = 0.0534 \quad y_{C_3H_6} = y_{CH_4} = 0.4461$$

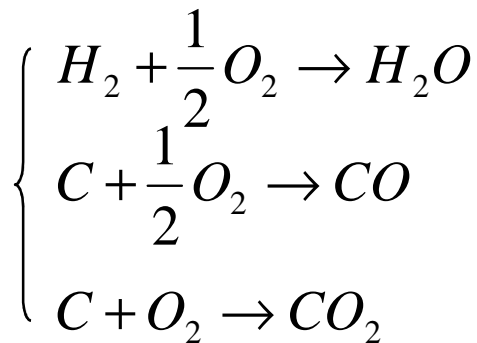
A bed of coal in a coal gasifier is fed with steam and air, and produce a gas stream containing  $H_2$ ,  $CO$ ,  $O_2$ ,  $H_2O$ ,  $CO_2$ , and  $N_2$ . If the feed to the gasifier consists of 1 mol of steam and 2.38 mol of air, calculate the equilibrium composition of the gas stream at  $P = 20$  bar for temperature 1000, 1100, 1200, 1300, 1400, and 1500 K.

---

The feed stream:

1 mol C,  $O_2 = (0.21)(2.38) = 0.5$  mol,  $N_2 = (0.79)(2.38) = 1.88$  mol

The formation reactions for the compounds are:



	$\Delta G_f^\circ$ J/mol		
T (K)	$H_2O$	$CO$	$CO_2$
1000	-192424	-200240	-395790
1100	-187000	-209110	-395960
1200	-181380	-217830	-396020
1300	-175720	-226530	-396080
1400	-170020	-235130	-396130
1500	-164310	-243740	-396160

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



$K = \dots$



Carbon is a pure solid phase:  $\frac{\hat{f}_C}{f_C^o} = \frac{f_C(@ 20 \text{ bar})}{f_C^o(@ 1 \text{ bar})} \approx 1$

Assuming ideal gases for the remaining species:

$$\prod_i (y_i)^{v_{i,j}} = \left(\frac{P}{P^o}\right)^{-v_j} K_j$$

$$K_I = \frac{y_{H_2O}}{\sqrt{y_{O_2} y_{H_2}}} \left(\frac{P}{P^o}\right)^{-1/2}$$

$$K_{II} = \frac{y_{CO}}{\sqrt{y_{O_2}}} \left(\frac{P}{P^o}\right)^{1/2}$$

$$K_{III} = \frac{y_{CO_2}}{y_{O_2}}$$

With a basis of 1 mol of C feed:

$$y_{H_2} = \frac{-\varepsilon_I}{3.38 + (\varepsilon_{II} - \varepsilon_I)/2}$$

$$y_{CO} = \frac{\varepsilon_{II}}{3.38 + (\varepsilon_{II} - \varepsilon_I)/2}$$

$$y_{CO_2} = \frac{\varepsilon_{III}}{3.38 + (\varepsilon_{II} - \varepsilon_I)/2}$$

$$y_{H_2O} = \frac{1 + \varepsilon_I}{3.38 + (\varepsilon_{II} - \varepsilon_I)/2}$$

$$y_{N_2} = \frac{1.88}{3.38 + (\varepsilon_{II} - \varepsilon_I)/2}$$

$$y_{O_2} = \frac{\frac{1}{2}(1 - \varepsilon_I - \varepsilon_{II}) - \varepsilon_{III}}{3.38 + (\varepsilon_{II} - \varepsilon_I)/2}$$

Three equations and three unknowns ... can be solved.

# Non- stoichiometric method

- Alternative method to solve chemical reaction equilibrium problems
  - base on the fact that the total Gibbs energy of the system has it minimum value
  - the basis for a general scheme of computer solution
  - $(G^t)_{T,P} = g(n_1, n_2, n_3, \dots n_N)$
  - Find the set  $\{n_i\}$  which minimizes  $G^t$  for specified T and P, subject to the constraints of the material balances.

# Lagrange's undetermined multiplier method

- The material balance on each element  $k$  :

$$\sum_i n_i a_{ik} = A_k$$

multiply the Lagrange multipliers

$$\lambda_k \left( \sum_i n_i a_{ik} - A_k \right) = 0$$

summed over  $k$

$$\sum_k \lambda_k \left( \sum_i n_i a_{ik} - A_k \right) = 0$$

$$F = G^t + \sum_k \lambda_k \left( \sum_i n_i a_{ik} - A_k \right)$$

$$F = G^t + \sum_k \lambda_k \left( \sum_i n_i a_{ik} - A_k \right)$$

F (and  $G^t$ ) minimum value?

$$\left( \frac{\partial F}{\partial n_i} \right)_{T,P,n_j} = \left( \frac{\partial G^t}{\partial n_i} \right)_{T,P,n_j} + \sum_k \lambda_k a_{ik} = 0 \quad (i = 1, 2, \dots, N)$$

$$\mu_i + \sum_k \lambda_k a_{ik} = 0 \quad (i = 1, 2, \dots, N)$$

$$\mu_i = G_i^o + RT \ln \left( \frac{\hat{f}_i}{f_i^o} \right)$$

gas phase reaction  
pure ideal gas

$$\mu_i = G_i^o + RT \ln \left( \frac{\hat{f}_i}{P^o} \right)$$

$$\mu_i = \Delta G_{fi}^o + RT \ln \left( \frac{y_i \hat{\phi}_i P}{P^o} \right)$$

$$\Delta G_{fi}^o + RT \ln \left( \frac{y_i \hat{\phi}_i P}{P^o} \right) + \sum_k \lambda_k a_{ik} = 0 \quad (i = 1, 2, \dots, N)$$

Calculate the equilibrium compositions at 1000 K and 1 bar of a gas-phase system containing the species CH<sub>4</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>, and H<sub>2</sub>. In the initial unreacted state, there are present 2 mol of CH<sub>4</sub> and 3 mol of H<sub>2</sub>O. Values of ΔG<sub>f</sub><sup>o</sup> at 1000 K of each species are given.

	Element <i>k</i>		
	C	O	H
	<i>A<sub>k</sub></i> = no. of atomic masses of <i>k</i> in the system		
	2	3	14
species	<i>a<sub>ik</sub></i> = no. of atoms of <i>k</i> per molecule of <i>i</i>		
CH <sub>4</sub>	1	0	4
H <sub>2</sub> O	0	1	2
CO	1	1	0
CO <sub>2</sub>	1	2	0
H <sub>2</sub>	0	0	2

$$\Delta G_{fi}^o + RT \ln \left( \frac{y_i \hat{\phi}_i P}{P^o} \right) + \sum_k \lambda_k a_{ik} = 0 \quad (i = 1, 2, \dots, N)$$

Ideal gas:  $\hat{\phi}_i = 1$        $\frac{P}{P^o} = 1$

$$\frac{\Delta G_{fi}^o}{RT} + \ln \left( \frac{n_i}{\sum_i n_i} \right) + \sum_k \frac{\lambda_k}{RT} a_{ik} = 0 \quad (i = 1, 2, \dots, N)$$

$$\frac{\Delta G_{fi}^o}{RT} + \ln\left(\frac{n_i}{\sum_i n_i}\right) + \sum_k \frac{\lambda_k}{RT} a_{ik} = 0 \quad (i = 1, 2, \dots, N)$$

For the 5 species:

$$\text{CH}_4: \quad \frac{19720}{RT} + \ln\left(\frac{n_{\text{CH}_4}}{\sum_i n_i}\right) + \frac{\lambda_C}{RT} + \frac{4\lambda_H}{RT} = 0$$

...

5 equations

For the 3 elements:

$$\text{C}: \quad n_{\text{CH}_4} + n_{\text{CO}} + n_{\text{CO}_2} = 2$$

$$\text{H}: \quad 4n_{\text{CH}_4} + 2n_{\text{H}_2\text{O}} + 2n_{\text{H}_2} = 14$$

$$\text{O}: \quad n_{\text{H}_2\text{O}} + n_{\text{CO}} + 2n_{\text{CO}_2} = 3$$

3 equations

$$\sum_i n_i = n_{\text{CH}_4} + n_{\text{H}_2\text{O}} + n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{H}_2}$$

1 equations

Solve  
simultaneously