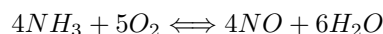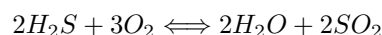**Problem 1:** Develop expressions for the mole fractions of reacting species as function of the reaction coordinate, ε, for:
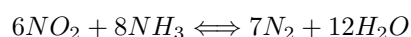
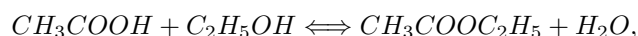(a) A system initially containing 2 moles of NH_3 and 5 moles of O_2:

$$4NH_3 + 5O_2 \Longleftrightarrow 4NO + 6H_2O$$

(b) A system initially containing 3 moles of H_2S and 5 moles of O_2:

$$2H_2S + 3O_2 \Longleftrightarrow 2H_2O + 2SO_2$$

(c) A system initially containing 3 moles of NO_2, 4 moles of NH_3 and 1 mole of N_2:

$$6NO_2 + 8NH_3 \Longleftrightarrow 7N_2 + 12H_2O$$

Problem 2: In the esterification reaction of acetic acid with ethanol at 100°C,

$$CH_3COOH + C_2H_5OH \Longleftrightarrow CH_3COOC_2H_5 + H_2O,$$

calculate the mass fraction of ethyl acetate given that initially there was 1 mole of acetic acid and ethanol. The reaction enthalpy and Gibbs energy at standard state (25°C and 1 atm) are $\Delta H_{298}^{\circ} = -3640$ J and $\Delta G_{298}^{\circ} = -4650$ J.

Problem 3: Give the equation for the stoichiometric combustion of 1 mole of general hydrocarbons, C_xH_y with O_2 producing CO_2 and water. Develop expressions for gas phase mole fractions of each species as a function of the reaction coordinate. Assume that initially 1 mole of hydrocarbon and the stoichiometric amount of oxygen for complete conversion are present.

Problem 4: In a reactor, 2 moles of CO_2, 5 moles of H_2 and 1 mole of CO are mixed and start to undergo the following reactions:

$$CO_2 + 3H_2 \quad \Longleftrightarrow \quad CH_3OH + H_2O$$
$$CO_2 + H_2 \quad \Longleftrightarrow \quad CO + H_2O$$
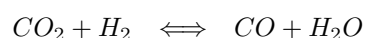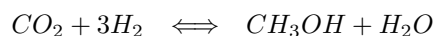
Develop expressions for the mole fractions of the reacting species as functions of the reaction coordinates for the two reactions.

Problem 5: For the ammonia synthesis reaction,

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \Longleftrightarrow NH_3$$
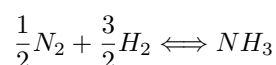
with 0.5 mole of N_2 and 1.5 moles of H_2 as the initial amounts of reactants and with the assumption that the equilibrium mixture is an ideal gas, show that

$$\varepsilon_e = 1 \pm \left(1 + 1.299K\frac{P}{P^{\circ}}\right)^{-0.5}$$

Problem 6: Assuming that all species and their mixtures are ideal gases, derive an equation for the Gibbs energy as a function of the reaction coordinate for the reaction below at 1000K.

$$H_2 + CO_2 \Longleftrightarrow H_2O + CO$$
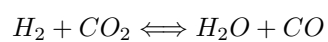
Given $\Delta G_f^\circ \left(\text{J.gmol}^{-1} \right)$ at 1000K: (a) H_2O: -192420, (b) CO: -200240 and (c) CO_2: -395790.

Problem 01:

a) 2 moles of NH_3 + 5 moles of O_2:

$$4NH_3 + 5O_2 \rightleftarrows 4NO + 6H_2O$$

$$\nu = \sum \nu_i = -4 - 5 + 4 + 6 = 1$$

$$M_0 = \sum M_{i,0} = 2 + 5 = 7$$

↑
initial number
of moles

$$y_i = \frac{M_i}{m} = \frac{M_{i,0} + \nu_i \varepsilon}{m_0 + \nu \varepsilon}$$

$$y_{NH_3} = \frac{2 - 4\varepsilon}{7 + \nu} \quad ; \quad y_{O_2} = \frac{5 - 5\varepsilon}{7 + \nu}$$

$$y_{NO} = \frac{4\varepsilon}{7 + \nu} \quad ; \quad y_{H_2O} = \frac{6\varepsilon}{7 + \nu}$$

b) 3 mols of H_2S + 5 mols of O_2:

$$2H_2S + 3O_2 \rightleftarrows 2H_2O + 2SO_2$$

$$\nu = -2 - 3 + 2 + 2 = -1 \qquad M_0 = 3 + 5 = 8$$

$$y_{H_2S} = \frac{3 - 2\varepsilon}{8 - \varepsilon} \;;\; y_{O_2} = \frac{5 - 3\varepsilon}{8 - \varepsilon} \;;\; y_{H_2O} = \frac{2\varepsilon}{8 - \varepsilon} \;;\; y_{SO_2} = \frac{2\varepsilon}{8 - \varepsilon}$$

c) 3 mols of NO_2 + 4 moles of NH_3 + 1 mol of N_2

$$6NO_2 + 8NH_3 \rightleftharpoons 7N_2 + 12H_2O$$
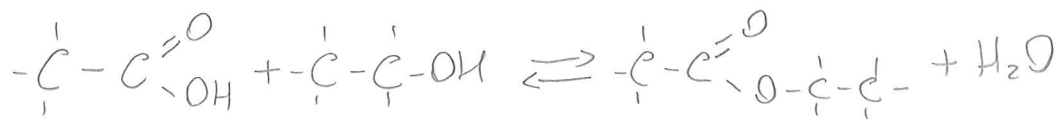
$\nu = -6 - 8 + 7 + 12 = 5$

$m_0 = 3 + 4 + 1 = 8$

$y_{NO_2} = \dfrac{3 - 6\varepsilon}{8 + 5\varepsilon}$; $y_{NH_3} = \dfrac{4 - 8\varepsilon}{8 + 5\varepsilon}$; $y_{N_2} = \dfrac{1 + 7\varepsilon}{8 + 5\varepsilon}$; $y_{H_2O} = \dfrac{12\varepsilon}{8 + 5\varepsilon}$

Problem 02:

$$-\overset{|}{\underset{|}{C}}-C\overset{\textstyle O}{\underset{\textstyle OH}{\diagup}} + -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH \rightleftharpoons -\overset{|}{\underset{|}{C}}-C\overset{\textstyle O}{\underset{\textstyle O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-}{\diagup}} + H_2O$$

Initially: $\begin{cases} 1\,mol \;\; HAc \\ 1\,mol \;\; EtOH \end{cases}$

$x_{EtAc} = ?$

$\begin{cases} \Delta U^\circ_{298} = -3640\,J \\ \Delta G^\circ_{298} = -4650\,J \end{cases}$

$$x_{EtAc} = \frac{\varepsilon}{2 + 0.\varepsilon} = \varepsilon/2 = x_{H_2O}$$

$$x_{HAc} = \frac{1-\varepsilon}{2} = x_{EtOH}$$

Assuming ideal solution

$$\prod_{i=1}^{c=4} x_i^{\nu} = K = x_{HAc}^{-1}\, x_{EtOH}^{-1}\, x_{EtAc}\, x_{H_2O} = \frac{x_{EtAc}\, x_{H_2O}}{x_{HAc}\, x_{EtOH}}$$

$$K = \frac{\varepsilon^2}{4}\frac{4}{(1-\varepsilon)^2} = \frac{\varepsilon^2}{(1-\varepsilon)^2} \rightsquigarrow$$

By calculating K, we can obtain ε and then $\underline{x_{EtAc}}$.

K can be calculated from

K is temperature-dependent!

$$\ln K_{298} = -\frac{\Delta G^\circ_{298}}{RT} = \frac{4650}{8.314 \times 298.15} = 1.8759$$

Now, in order to calculate K at 373.15 K (100°C)
we can use the van't Hoff Equation

$$\frac{d(\ln K)}{dT} = -\frac{\Delta U^{\circ}_{298}}{RT^2}$$

$$\int_{K_{298}}^{K_{373}} d(\ln K) = -\int_{298.15}^{373.15} \frac{\Delta U^{\circ}_{298}}{RT^2} dT$$

$$\ln\left(\frac{K_{373}}{K_{298}}\right) = -\frac{\overset{-3640\,J}{\Delta U^{\circ}_{298}}}{R}\left(\frac{1}{373.15} - \frac{1}{298.15}\right) = -0.2951$$

$$\boxed{K_{373} = 4.8586}$$

$$K_{373} = 4.8586 = \frac{\varepsilon^2}{(1-\varepsilon)^2} \quad \therefore \quad \varepsilon = 0.6879$$

Now

$$\boxed{\chi_{EtAc} = \frac{\varepsilon}{2} = 0.34395}$$

Problem 3:

$$C_x H_y + (x + y/4) O_2 \rightleftharpoons x CO_2 + y/2 H_2 O$$
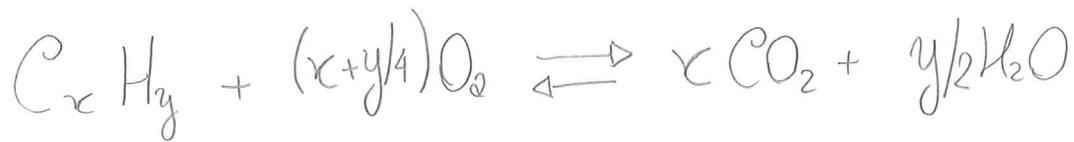
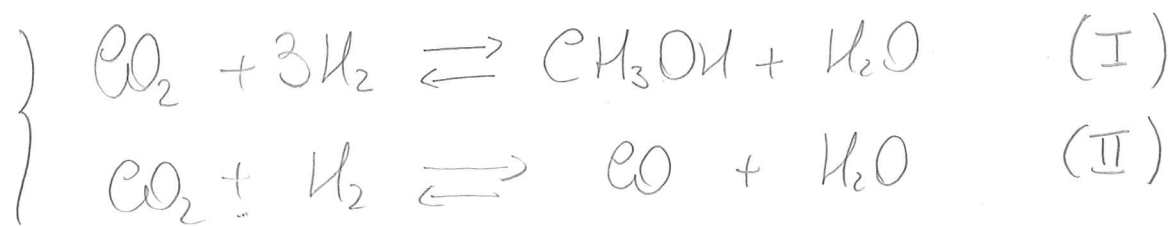$$\nu = -1 - \left(x + \frac{y}{4}\right) + x + \frac{y}{2} = y/4 - 1$$

$$n_0 = 1 + (x + y/4)$$

$$y_{C_x H_y} = \frac{1 - \varepsilon}{(1 + x + y/4) + (y/4 - 1)\varepsilon} \quad ; \quad y_{O_2} = \frac{(x + y/4) - (x + y/4)\varepsilon}{(1 + x + y/4) + (y/4 - 1)\varepsilon}$$

$$y_{CO_2} = \frac{x\varepsilon}{(1 + x + y/4) + (y/4 - 1)\varepsilon} \quad ; \quad y_{H_2O} = \frac{y/2 \varepsilon}{(1 + x + y/4) + (y/4 - 1)\varepsilon}$$

Problem 4

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (I)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (II)$$

Initial :
$\begin{cases} 2 \text{ moles of } CO_2 \\ 5 \text{ moles of } H_2 \\ 1 \text{ mole of } CO \end{cases}$

i \ j	CO_2	H_2	CH_3OH	CO	H_2O	ν_j
I	-1	-3	1	0	1	-2
II	-1	-1	0	1	1	0

$$m_0 = 2 + 5 + 1 = 8 \qquad\qquad y_i = \dfrac{m_{i,0} + \sum_j \nu_{ij} \varepsilon_j}{m_0 + \sum_j \nu_j \cdot \varepsilon_j}$$
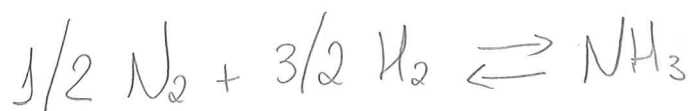
$$y_{CO_2} = \frac{2 - \varepsilon_I - \varepsilon_{II}}{8 - 2\varepsilon_I} \quad ; \quad y_{H_2} = \frac{5 - 3\varepsilon_I - \varepsilon_{II}}{8 - 2\varepsilon_I}$$

$$y_{CH_3OH} = \frac{\varepsilon_I}{8 - 2\varepsilon_I} \quad ; \quad y_{CO} = \frac{1 + \varepsilon_{II}}{8 - 2\varepsilon_I}$$

$$y_{H_2O} = \frac{\varepsilon_I + \varepsilon_{II}}{8 - 2\varepsilon_I}$$

Problem 5

$$\tfrac{1}{2} N_2 + \tfrac{3}{2} H_2 \rightleftharpoons NH_3$$

Initial: 0.5 mole N_2
1.5 moles H_2

Show: $\varepsilon_e = 1 - \left(1 + 1.299 \, K \, P/p_0\right)^{-0.5}$

$m_0 = 0.5 + 1.5 = 2$

$\nu = -1/2 - 3/2 + 1 = -1$

$$y_i = \frac{m_{i,0} + \nu_i \varepsilon}{m_0 + \nu \varepsilon}$$

$$y_{N_2} = \frac{1/2 - 1/2 \varepsilon}{2 - \varepsilon} = \frac{1/2(1-\varepsilon)}{2-\varepsilon}; \quad y_{H_2} = \frac{3/2 - 3/2 \varepsilon}{2 - \varepsilon} = \frac{3/2(1-\varepsilon)}{2-\varepsilon}$$

$$y_{NH_3} = \frac{\varepsilon}{2-\varepsilon}$$

For gas phase the equilibrium constant is defined as:

$$\prod_{i=1}^{c} (\phi_i y_i)^{\nu_i} = K (P/P_0)^{-\nu}$$

Assuming the mixture behaves as an ideal gas, $\phi_i = 1$

$$\prod_{i=1}^{c} y_i^{\nu_i} = K \left(P/P_0 \right)^{-\nu}$$

$$y_{N_2}^{-1/2} \, y_{H_2}^{-3/2} \, y_{NH_3} = K \left(\frac{P}{P_0} \right)$$

$$\frac{y_{NH_3}}{y_{N_2}^{1/2} \, y_{H_2}^{3/2}} = \frac{\mathcal{E}/2 - \mathcal{E}}{\left[\frac{1/2(1-\mathcal{E})}{2-\mathcal{E}} \right]^{1/2} \left[\frac{3/2(1-\mathcal{E})}{2-\mathcal{E}} \right]^{3/2}} = K \left(P/P_0 \right)$$

$$\frac{\mathcal{E}(2-\mathcal{E})}{(1-\mathcal{E})^2 (1/2)^{1/2} (3/2)^{3/2}} = K \left(P/P_0 \right)$$

$$\frac{\mathcal{E}(2-\mathcal{E})}{(1-\mathcal{E})^2} = \underbrace{\left(\frac{1}{2} \right)^{1/2} \left(\frac{3}{2} \right)^{3/2}}_{1.2990} K \left(P/P_0 \right)$$

$$\underbrace{\hspace{3cm}}_{\Gamma}$$

$$2\mathcal{E} - \mathcal{E}^2 = (1 - 2\mathcal{E} + \mathcal{E}^2) \Gamma = \Gamma - 2\Gamma\mathcal{E} + \Gamma\mathcal{E}^2$$

$$\mathcal{E}^2 (1 + \Gamma) + (-2\Gamma - 2)\mathcal{E} + \Gamma = 0$$

$$\mathcal{E} = \frac{-(-2\Gamma - 2) \pm \sqrt{(-2\Gamma - 2)^2 - 4(1 + \Gamma)\Gamma}}{2(1 + \Gamma)}$$

$$\mathcal{E} = \frac{-(-2\Gamma-2) \pm \sqrt{4\Gamma^2 + 8\Gamma + 4 - 4\Gamma - 4\Gamma^2}}{2(1+\Gamma)}$$

$$\mathcal{E} = \frac{(2\Gamma+2) \pm \sqrt{4 \cdot (\Gamma+1)}}{2(1+\Gamma)} = \frac{2(1+\Gamma) \pm 2\sqrt{1+\Gamma}}{2(1+\Gamma)}$$
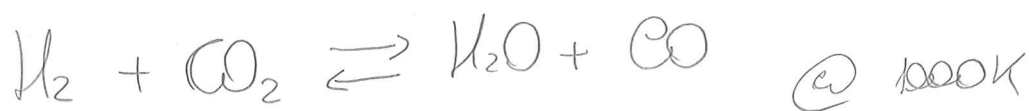
$$\mathcal{E} = \frac{(1+\Gamma)\left[1 \pm (1+\Gamma)^{-1/2}\right]}{1+\Gamma} = 1 \pm (1+\Gamma)^{-1/2}$$

with

$$1 + \Gamma = 1 + 1.299 \, K \, (P/P_0)$$

Problem 6 $\quad (T = 1000 K)$

$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$

@ 1000K

$\Delta G^\circ_{f, H_2O} = -192420\ J/_{gmol}$

$\Delta G^\circ_{f, CO} = -200240\ J/_{gmol}$

$\Delta G^\circ_{f, CO_2} = -395790\ J/_{gmol}$

$$G = \sum y_i G_i + RT \sum y_i \ln y_i$$

$$G = \sum y_i \Delta G^\circ_{f,i} + RT \sum y_i \ln y_i$$

$$dG^t = d(mG) = m\frac{dG}{d\varepsilon} + G\frac{dm}{d\varepsilon} = 0$$

$\rightarrow$ $dG/d\varepsilon = 0$ (equilibrium)

$\hookrightarrow dm = 0 \rightarrow$

Assuming that initially there is 1 mole of H_2 and CO_2

$$y_{H_2} = \frac{1-\varepsilon}{2} = y_{CO_2} \quad ; \quad y_{H_2O} = \frac{\varepsilon}{2} = y_{CO}$$

$$G = \left(y_{H_2} \Delta G^\circ_{f, H_2} + y_{CO_2} \Delta G^\circ_{f, CO_2} + y_{H_2O} \Delta G^\circ_{f, H_2O} + y_{CO} \Delta G^\circ_{f, CO} \right) +$$

$$RT \left(y_{H_2} \ln y_{H_2} + y_{CO_2} \ln y_{CO_2} + y_{H_2O} \ln y_{H_2O} + y_{CO} \ln y_{CO} \right)$$

$$\boxed{\Delta G^\circ_{f, H_2} = 0}$$

$$G = \left[\frac{1-\varepsilon}{2}\left(-395790 \frac{J}{g\,mol}\right) + \frac{\varepsilon}{2}\left(-192420 - 200240\right) \frac{J}{g\,mol}\right] +$$

$$RT\left[(1-\varepsilon)\ln\left(\frac{1-\varepsilon}{2}\right) + \varepsilon\ln\left(\frac{\varepsilon}{2}\right)\right]$$

$$\frac{dG}{d\varepsilon} = -A + B - RT\ln\left(\frac{1-\varepsilon}{2}\right) - RT + RT\ln(\varepsilon/2) + RT$$

$$\frac{dG}{d\varepsilon} = B - A + RT\left[\ln(\varepsilon/2) - \ln\left(\frac{1-\varepsilon}{2}\right)\right] = 0$$

where $A = \dfrac{-395790}{2} = -197895.0$

$B = \dfrac{-192420 - 200240}{2} = -196330.0$

$$\ln\left[\frac{\varepsilon/2}{(1-\varepsilon)/2}\right] = -0.1882$$

$$\boxed{\varepsilon = 0.4531}$$

(@ equilibrium)