

Lecture 1C: Examples of Chemical Equilibrium Calculation

Reaction System: $2 SO_2 + O_2 = 2 SO_3$

Conditions: $T = 600^\circ C = 873^\circ K$

$P = 1 atm$

Stoichiometric Feed

No Nitrogen

Calculate equilibrium conversion of SO_2 . Conversion of 99% is desired.

Species Names	No.	Stoich. Coeff.	$\frac{k cal}{mol}$ $\frac{\Delta G_f}{\Delta H_f}$	n_{jo}	$n_j = n_{jo} + \nu_j X$
SO_2	1	-2	-71.7	-70.9	$2 - 2X$
O_2	2	-1	0	0	$1 - 1X$
SO_3	3	2	-88.6	-94.4	$0 + 2X$
<hr/>		$S = 3$	$\sum \nu_j = -1$	$\sum n_{jo} = 3n_{tot} = \sum n_j = 3 - x$	

Assume ideal gas mixture.

$$K = K_y \left(\frac{P}{P_o} \right)^{\sum \nu_j} = K_y \left(\frac{P}{P_o} \right)^{-1} = K_y \left(\frac{P_o}{P} \right) \quad (A)$$

$$K_y = \prod y_j^{\nu_j} = y_1^{-2} y_2^{-1} y_3^2 = \frac{y_3^2}{y_1^2 y_2} = \left(\frac{y_{SO_3}^2}{y_{SO_2}^2 y_{O_2}} \right)$$

Now

$$y_1 = \frac{n_1}{n_{tot}} = \frac{2 - 2X}{3 - X} \quad y_2 = \frac{1 - X}{3 - X} \quad y_3 = \frac{2X}{3 - X}$$

$$K_y = \frac{4 X^2}{(3 - X)^2} = \frac{x^2 (3 - X)}{4 (1 - X)^2 (1 - X)} = \frac{x^2 (3 - X)}{(1 - X)^3}$$

where $X = X_e = \text{equilibrium extent}$

From (A)

$$\frac{x^2 (3 - x)}{(1 - x)^3} = K_{873} \left(\frac{P}{P_o} \right) \quad (\text{B})$$

Calculate K_{298} at 298 K

$$\Delta G_r^\circ = (-2) \times (-71.7) + (-1) \times (0) + 2 \times (-88.6) = -33.8 \frac{\text{k cal}}{\text{mol}}$$

$$K_{298} = e^{\frac{\Delta G_r^\circ}{RT_o}} = e^{\frac{-33,800}{1.987 \times 298}} = e^{57.08} = 6.17 \times 10^{24}$$

Calculate ΔH_r , K_{873}

$$\Delta H_r^\circ = (-2) \times (-70.9) + (1) \times (0) + 2 \times (-94.4) = -47.0 \frac{\text{k cal}}{\text{mol}}$$

Assume for simplicity (in order to find a first estimate for equilibrium conditions) that $\Delta H_r \approx \text{const} \approx \Delta H_r^\circ$

Then

$$\frac{d \ln K}{dT} = \frac{\Delta H_r^\circ}{RT^2}; \text{ and at } T = T_o = 298, \quad K = K_{298}$$

$$\ln \left(\frac{K_T}{K_{298}} \right) = \frac{\Delta H_r^\circ}{R} \left(\frac{1}{298} - \frac{1}{T} \right)$$

$$K_T = K_{298} e^{\frac{\Delta H_r^\circ}{R} \left(\frac{1}{298} - \frac{1}{T} \right)}$$

$$K_{873} = e^{57.08} - \frac{47,000}{1.987} \left(\frac{1}{298} - \frac{1}{873} \right) = e^{4.80}$$

$$\underline{K_{873} = 121.78}$$

Note the dramatic drop in K with temperature due to the exothermicity of the reaction ($\Delta H_r < 0$). While equilibrium would have been all the way to the right at 298 K we cannot operate at such conditions because the rate is too low.

Let us see what are the equilibrium limitations at 873 K.

Solve by trial and error equation (B) for equilibrium extent X.

$$\frac{X^2 (3 - X)}{(1 - X)^3} = K_{873} \left(\frac{P_o}{P} \right)^{-1} \quad (C)$$

where $K_{873} = 121.78$; $\frac{P}{P_o} = 1$

Rearrange to use Newton-Raphson procedure

$$\begin{aligned} \phi(x) &= 0 = X^2 (3 - X) - 121.78 (1 - X)^3 \\ D\phi(x) &= 2X (3 - X) - X^2 + 3 \times 121.78 (1 - X)^2 \\ X_{n+1} &= X_n \frac{\phi(X_n)}{D\phi(X_n)} \end{aligned} \quad (C)$$

Using a starting guess of $X_o = 0.5$ the Newton Raphson algorithm (C) yields:

Iteration No	n = 0	1	2	3	4	5
Extent	0.5	0.656	0.742	0.773	0.777	0.777

$$X = X_e = 0.777 \text{ (mol)}$$

Conversion of SO_2 is:

$$\begin{aligned} x_{SO_2} &= \frac{n_{SO_2,0} - n_{SO_2}}{n_{SO_2,0}} = \frac{2 - (2 - 2X)}{2} = \frac{2X}{2} = X \\ x_{SO_2,eq} &= 0.777 \ll 0.99 \end{aligned}$$

Equilibrium conversion of 0.99 cannot be reached under these conditions.

Equilibrium extent could be increased by:

- lowering the temperature (but rates are lower)
- increasing the pressure (some of it can be recovered by running a turbine at the end of reactor as done in the former USSR)

Examine for yourself the effect of T and P.

What effect would use of air instead of pure oxygen have? Would that increase or decrease equilibrium conversion at our $T = 873 \text{ K}$ and $P = 1 \text{ atm}$?