Physical Gas Dynamics (Ph 5300)

Exe # 2

we have 6 unknowns and there are two type of atoms,

que-2: equations -

$$H_2 \rightleftharpoons 2H \quad \text{— ①}$$

$$O_2 \rightleftharpoons 2O \quad \text{— ②}$$

$$H + O \rightleftharpoons OH \quad \text{— ③}$$

$$OH + H \rightleftharpoons H_2O \quad \text{— ④}$$

at equilibrium → P_t : total Pressure

$$Kp_1 = \frac{P_H^2}{P_{H_2}} = \frac{(P_t \cdot X_H)^2}{(P_t \cdot X_{H_2})} \quad \text{(i)}$$

$$Kp_2 = \frac{P_O^2}{P_{O_2}} = \frac{(P_t X_O)^2}{(P_t X_{O_2})} \quad \text{— (ii)}$$

$$Kp_3 = \frac{P_{OH}}{P_O P_H} = \frac{(P_t X_{OH})}{(P_t^2 X_O X_H)} \quad \text{— (iii)}$$

$$Kp_4 = \frac{P_{H_2O}}{P_{OH} P_H} = \frac{P_t (X_{H_2O})}{P_t^2 X_{OH} X_H} \quad \text{— (iv)}$$

Atom balance eqn. →

$$\left[2 \cdot N^0_{H_2} + 1 \cdot N^0_H + 1 \cdot N^0_{OH} + 2 \cdot N^0_{H_2O}\right]_{t=0} = \left[2 \cdot N_{H_2} + 1 \cdot N_H + 1 \cdot N_{OH} + 2 \cdot N_{H_2O}\right]_{\text{at equilibrium}}$$

(N^0 ← at t=0)

— (v)

→

Since total number of atoms will always be conserved. for 'H' & 'O'.

$$\left[2\cdot N^0_{O_2} + 1\cdot N^0_O + 1\cdot N^0_{OH} + 1\cdot N^0_{H_2O}\right]_{\text{initial atoms of 'O'}}$$

$$= \left[2\cdot N_{O_2} + 1\cdot N_O + 1\cdot N_{OH} + 1\cdot N_{H_2O}\right]_{\text{at equili.}} \quad \text{——— (vi)}$$

we can convert the above eqn as following by using (v) and (vi) →

(v) ÷ (vi)

$$\Rightarrow \left(\frac{2\, N^0_{H_2} + 1\cdot N^0_H + 1\cdot N^0_{OH} + 2\cdot N^0_{H_2O}}{2\, N^0_{O_2} + 1\cdot N^0_O + 1\cdot N^0_{OH} + 1\cdot N^0_{H_2O}}\right)$$

$$= \left(\frac{2\cdot P_{H_2} + P_H + P_{OH} + 2P_{H_2O}}{2P_{O_2} + P_O + P_{OH} + P_{H_2O}}\right)_{\text{at equ.}}$$

we have six equations and six unknowns can be solved using matlab.

use $P_{H_2} + P_H + P_O + P_{O_2} + P_{OH} + P_{H_2O} = P_{total}$

$$\hookrightarrow \equiv X_{H_2} + X_H + X_O + X_{O_2} + X_{OH} + X_{H_2O} = 1$$

ques-3. (3)

eqns -

$$N_2 \rightleftharpoons 2N \quad \text{--- (1)}$$

$$O_2 \rightleftharpoons 2O \quad \text{--- (2)}$$

$$N + O \rightleftharpoons NO \quad \text{--- (3)}$$

$$NO + \tfrac{1}{2}O_2 \rightleftharpoons NO_2 \quad \text{--- (4)}$$

$$Kp_1 = \frac{P_N^2}{P_{N_2}} \quad \text{--- (i.)}$$

$$Kp_2 = \frac{P_O^2}{P_{O_2}} \quad \text{--- (ii.)}$$

$$Kp_3 = \frac{P_{NO}}{P_N \; P_O} \quad \text{--- (iii.)}$$

$$Kp_4 = \frac{P_{NO_2}}{P_{NO} * \sqrt{P_{O_2}}} \quad \text{--- (iv.)}$$

equations of atom balance →

use →
$\sum P_i = P_{total}$
or $P_{N_2} + P_{O_2} + P_N + P_O + P_{NO} + P_{NO_2} = P_t$ --- (V)

$$\left(2 \cdot N^0_{N_2} + 1 \cdot N^0_N + 1 \cdot N^0_{NO} + 1 \cdot N^0_{NO_2}\right) = 2 \cdot N_{N_2} + 1 \cdot N_N + 1 \cdot N_{NO} + 1 \cdot N_{NO_2} \quad \text{--- ~~(V.)~~}$$

$$\frac{2 \cdot N^0_{N_2} + 1 \cdot N^0_N + 1 \cdot N^0_{NO} + 1 \cdot N^0_{NO_2}}{2 \cdot N^0_{O_2} + 1 \cdot N^0_O + 1 \cdot N^0_{NO} \cdot 2 \cdot N^0_{NO_2}} = \frac{2P_{N_2} + P_N + P_{NO} + P_{NO_2}}{2P_{O_2} + P_O + P_{NO} + 2P_{NO_2}}$$

at equi.

--- (vi.)

Qu- 1.

$$CO + \frac{1}{2} O_2 \rightleftharpoons CO_2$$

initially: 1   1   1

at equi. $1-x$ $1-x/2$ $1+x$

$$P_{CO} = \left(\frac{1-x}{3-x/2}\right) \times P_t$$

$$P_{O_2} = \left(\frac{1-x/2}{3-x/2}\right) \times P_t$$

$$P_{CO_2} = \left(\frac{1+x}{3-x/2}\right) P_t$$

(a) at $P_t = 1\,atm$, $T = 300\,K$.

$$K_P = \frac{P_{CO_2}\,(P_{ref})^{1/2}}{P_{CO}\,(P_{O_2})^{1/2}};$$

Since $P_{ref} = 1$

$$\therefore K_P = \frac{P_{CO_2}}{P_{CO}\cdot(P_{O_2})^{1/2}}$$

Note: "K_P" is unitless quantity.

also $K_P = e^{-\frac{\Delta G_{rxn}(T)}{RT}}$

calculating ΔG_{rex} at 300K →

$$\Delta G = 1\cdot\hat{g}_{CO_2} - 1\cdot\hat{g}_{CO} - \frac{1}{2}\hat{g}_{O_2}$$

$$= (\hat{h}_{CO_2} - T\hat{s}_{CO_2}) - (\hat{h}_{CO} - T\hat{s}_{CO}) - \frac{1}{2}(\hat{h}_{O_2} - T\hat{s}_{O_2})$$

$$= \left\{(69 - 393.522\times10^3) - 300\times214.025\right\} - \left\{(54 - 110.527\times10^3) - 300\times197.653\right\}$$

$$- \frac{1}{2}\left\{(54+0) - 300\times205.329\right\}$$

$$\Delta G = (-457660.5) - (-169760.9) - \frac{1}{2}(-61544.7)$$

$$\Delta G = -457660.5 + 169760.9 + 30772.35$$

$$\Delta G = -257119.25 \ \text{J/mol}$$

$$K_p = e^{-\left\{\frac{-257119.25}{8.31 \times 300}\right\}}$$

$$\boxed{K_p = e^{+103.136}} \rightarrow \infty$$

$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$$

equilibrium will shift towards forward direction.

Since CO is limiting agent therefore it will be almost equal to zero.

$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$$

	CO	$\frac{1}{2}O_2$	CO_2
initial	1	1	1
at equi.	$1-1$	$1-\frac{1}{2}$	$1+1$
	0	$\frac{1}{2}$	2

$$X_{CO} = 0, \quad X_{O_2} = \frac{1/2}{2.5} = \frac{1}{5} = 0.2$$

$$X_{CO_2} = 1 - (0.2 + 0) = 0.8$$

(b) In our equilibrium calculations we solve for final state which is equilibrium, starting from one given state. we do not talk about the kinetics of the process.

therefore in real life, the rate of reaction in the forward direction will be extremely low ~~to~~ and we have to wait for infinitely long in order to achieve equilibrium.

(c) $T = 1000K$; $P_{total} = 2$ atm.

$$Kp = e^{-\left(\frac{\Delta G_{rxn}}{RT}\right)}.$$

$$\Delta G\Big|_{1000K} = \left\{(33397 - 393522) - (1000 \times 269.299)\right\}$$

$$- \left\{(21690 - 110527) - (1000 \times 234.538)\right\}$$

$$- \frac{1}{2}\left\{(22703 + 0) - (1000 \times 243.578)\right\}$$

$$\Delta G\Big|_{1000K} = -629424 - (-323375) - (110437.5)$$

$$= -195611.5 \text{ Joules/mole}$$

$$Kp\Big|_{1000K} = e^{\frac{195611.5}{8.31 \times 1000}}$$

$$= \underbrace{e^{23.539}}_{\text{very high value}} \longrightarrow \infty$$

∴ the equilibrium will shift in the forward direction and there will not be any CO left.

$$x_{CO} = 0$$

$$x_{O_2} = 0.2$$

$$x_{CO_2} = 0.8$$

(d) $T = 3000K$ & $P_{total} = 2$ bar.

$$\Delta G\Big|_{3000K} = \left\{ (152852 - 393522) - 3000 \times 334.169 \right\}$$

$$- \left\{ (93546 - 110527) - 3000 \times 273.623 \right\}$$

$$- \frac{1}{2} \left\{ (98013 + 0) - 3000 \times 284.466 \right\}$$

$$\Delta G\Big|_{3000K} = -1243177 - (-837850) - (-377692.5)$$

$$= -27634.5 \text{ J/mol}$$

$$Kp\Big|_{3000K} = e^{\left(\frac{27634.5}{8.31 \times 3000}\right)}$$

$$= e^{1.10848} \simeq e^{1.1} = 3$$

Putting in equi. eqn →

$$3 = \frac{\left(\frac{1+x}{3-x/2}\right) \times \cancel{P_t}}{\left(\frac{1-x}{3-x/2}\right) \times \cancel{P_t} \sqrt{\left(\frac{1-x}{3-x/2}\right) P_t}}$$

Squaring both the sides,

$$\Rightarrow 9 = \frac{(1+x)^2}{(1-x)^2} \times \frac{(3-x/2)}{(1-x) * 2}$$

$$\Rightarrow 2 * 9 (1-x)^2 (1-x) = (1+x)^2 \frac{(6-x)}{2}$$

$$\Rightarrow 36 (1-x)^3 = (1+x)^2 (6-x)$$

$$\Rightarrow 36(1-3x+3x^2-x^3) = -x^3 + 4x^2 + 11x + 6$$

$$\Rightarrow 35x^3 - 104x^2 + 119x - 30 = 0$$

on Solving using matlab we get,

$$\boxed{x = 0.302}$$

(mole fraction) @ equilibrium

$$x_{CO} = \left(\frac{1-x}{3-x/2}\right) = 0.22$$

$$x_{O_2} = 0.29$$

$$x_{CO_2} = 0.49$$

(e) Now $T = 3000K$, $P_{total} = 5$ atm.

'Kp' will remain same as in part (d).

$$K_p = \frac{P_{CO_2}}{P_{CO}\sqrt{P_{O_2}}}$$

$$K_p = \frac{x_{CO_2}}{\sqrt{x_{O_2}}\, x_{CO}} \times \frac{1}{\sqrt{P_t}}$$ — this will make the difference.

(x_{CO}: mole fraction of CO)

$$3 = \frac{(1+x)\sqrt{3-x/2}}{(1-x)\sqrt{1-x}} \times \frac{1}{\sqrt{5}}$$

Solving this eq will give the following sol^n s.

mole fractions @ equilibrium:

$x_{CO_2} = 0.57$

$x_{O_2} = 0.27$

$x_{CO} = 0.16$

$CO + \frac{1}{2}O_2 \rightarrow CO_2 + \text{Heat}$ (exothermic)

(f) from previous solutions we can say following,

as we ↑ the temp. the reaction follows backward path,

And as we ↑ the pressure, the equilibrium shifts in the forward direction

which means the above reaction follows Le chatelier's Principle.

4. How will you solve the problem if the system in q3 is taken from a particular pressure 'P1' to a new pressure 'P2' through external work, keeping the temperature 'T' the same?

Soln:

Nothing special!

Solve the same set of equations for the new Pt, and the same T.

No special considerations needed.