**ENCH 501** F18 **Quiz #2** Name/ID: ____________________

October 2, 2018 Time Allowed: **45 minutes** Only Cheat Sheet permitted. aJ

Methanol is reformed by adding steam to produce hydrogen and carbon dioxide. The process has applications for the emerging fuel cell technology as substantial amounts of methanol can be safely stored as liquid, vaporized and reformed, and the hydrogen produced fed into large, stationary fuel cell arrays to produce electricity. The reaction is

$$CH_3OH_{(g)} + H_2O_{(g)} \leftrightarrow CO_2 + 3H_2$$

For this reaction, 500K is optimum for hydrogen production with excess steam, and at low pressures. The heats of formation and reaction are usually given at standard conditions of 25°C and the heats of formation of elements are arbitrarily set to zero. At elevated temperatures, the heats of formation of the various compounds are different from the values at 25°C, and elements have non-zero enthalpies. The heat of reaction is properly estimated at the temperature of the reaction. Some values of heats of formation are provided in the table below, all obtained in the same laboratory.

Into a closed vessel, 1 mole of methanol and 1.5 moles of steam were charged. The pressure is kept at 10 atm. and the temperature at 500K. The composition of the gas mixture at equilibrium is given in the table below. For the questions below, show your steps.

a) **(10 pts.)** If the temperature is suddenly dropped to and maintained at 450K but the pressure is maintained at 10 atm, what would the <u>number of moles of hydrogen</u> be at equilibrium and the uncertainty in the value?
b) **(Bonus: 2 pts)** If the mixture above is contained in a vessel with a piston, its temperature maintained at 500K, and the volume is increased until the pressure decreased from 10 to 4 atm, what would the equilibrium composition of the compounds now be in the vessel? Compare the results.

| Substance | $\Delta H_f$, 298.15K, kJ/mol | $\Delta H_f$, 450 - 500K, kJ/mol | Mole fractions at Equilibrium, T=500K, P=10atm, Molar Feed ratio $H_2O$:$CH_3OH$ is 1.5: 1 |
|---|---|---|---|
| $CH_3OH$ g | -200.71 ± 0.16 | -174.83 ± 1.41 | 0.018 |
| $H_2O$ g | -241.818 ± 0.033 | -234.055 ± 0.533 | 0.12 |
| $CO_2$ | -393.51 ± 0.13 | -384.25 ± 0.23 | 0.21 |
| $H_2$ | 0 | 6.61 ± 0.11 | 0.652 |

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The reaction is

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2$$

| | $CH_3OH$ | $H_2O$ | $CO_2$ | $H_2$ |
|---|---|---|---|---|
| $\Delta H_f$ 450–500K kJ/mol | −174.83 ± 1.41 | −234.055 ± 0.533 | −384.25 ± 0.23 | 6.61 ± 0.11 |

The heat of reaction is given by

$$\Delta H_r = \{-384.25 + 3(6.61)\} - \{-174.83 - 234.055\}$$

$$= 44.465 \text{ kJ/mole}$$ (lower than 49.02 kJ/mol at 25°C)

Since the data were obtained in the same lab, we assume the data is correlated.

$$\therefore \Delta(\Delta H_r) = 0.23 + 3(0.11) + 0.533 + 1.41$$

$$= \pm 2.503 \text{ kJ/mol}$$

From the data provided at equilibrium — 500K, 10 atm and $H_2O : CH_3OH$ ratio of 1.5 : 1, the equilibrium constant is

$$K_p = \frac{\bar{P}_{CO_2}\bar{P}_{H_2}^3}{\bar{P}_{CH_3OH}\bar{P}_{H_2O}} = \frac{y_{CO_2}y_{H_2}^3}{y_{CH_3OH}y_{H_2O}} \cdot P_t^2$$

$$= \frac{(0.21)(0.652)^3}{(0.018)(0.12)}(100) = 2694.687 \text{ atm}^2$$

(a) When the temperature drops, the equilibrium constant changes. From the Van't Hoff equation,

$$\ln \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H_r}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

But there is an error for $\Delta H_r$. The lower value is $44.465 - 2.503 = 41.962 \ kJ/mol$

and the upper value is $44.465 + 2.503 = 46.968 \ kJ/mol$

Using the lower $\Delta H_r$.

$$\ln \frac{K_{P_2}}{2694.687} = \frac{41.962(10^3)}{8.314}\left[\frac{1}{500} - \frac{1}{450}\right]$$

$$K_{P_2} = 2694.687\,(0.325762)$$
$$= 877.826 \ atm^2$$

The reaction has excess steam. Let $x$ be the number of moles of $CO_2$ at $=m$.

| | $CH_3OH$ | + $H_2O$ | $\rightleftharpoons CO_2$ | $+ 3H_2$ | $\Sigma$ mols |
|---|---|---|---|---|---|
| $t=0$ | 1 | 1.5 | 0 | 0 | 2.5 |
| $t_{=m}$ | $1-x$ | $1.5-x$ | $x$ | $3x$ | $2.5+2x$ |

$\therefore \quad y_{H_2} = \frac{3x}{2.5+2x}, \quad y_{CO_2} = \frac{x}{2.5+2x}, \quad y_{H_2O} = \frac{1.5-x}{2.5+2x}$

and $y_{CH_3OH} = \frac{1-x}{2.5+2x}.$

$$\therefore \quad K_p = \frac{\left(\frac{x}{2.5+2x}\right)\left(\frac{3x}{2.5+2x}\right)^3}{\left(\frac{1-x}{2.5+2x}\right)\left(\frac{1.5-x}{2.5+2x}\right)} \cdot P_t^2$$

$$\therefore \quad 877.826 = \frac{27x^4}{(1-x)(1.5-x)(2.5+2x)^2}(100)$$

$$\text{or} \quad 0.32512 = \frac{x^4}{(1-x)(1.5-x)(2.5+2x)^2}$$

lower $\Delta H_r$ value $\quad x = 0.8557$

When $\Delta H_r = 46.968$ kJ/mol, similar to above,

$$K_{P_2} = (2694.687)(0.28496)$$
$$= 767.888 \ \text{atm}^2$$

$$\text{or} \quad 0.2844 = \frac{x^4}{(1-x)(1.5-x)(2.5+2x)^2}$$

higher $\Delta H_r$ value

$x = 0.8445$

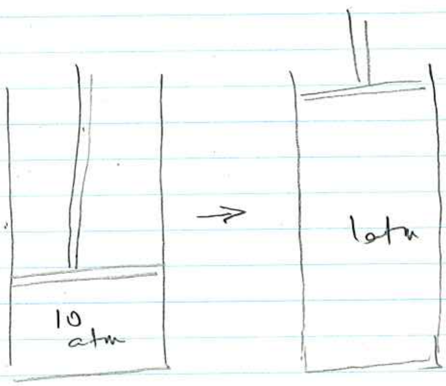
Expected $x = \bar{x} \pm \Delta x$ ; $\quad \bar{x} = 0.8501$, $\Delta x = 0.0056$

moles $H_2 = 2.5503 \pm 0.0168$ ⟶

at = "
at 450 K

(b) Bonus question

Since the temperature is maintained, from van't Hoff eq.




$$\ln \frac{Kp_2}{Kp_1} = \frac{\Delta H_r}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = 0$$

$$\therefore \; Kp_2 = Kp_1$$

For the conditions given,

$$Kp_2 = Kp_1 = 2694.687$$

But $Kp_2 = \dfrac{y_{CO_2}\, y_{H_2}^3}{y_{CH_3OH}\, y_{H_2O}} P_t^2$ and $P_t = 4$ atm

$$\therefore \; \frac{2694.687}{16} = \frac{27x^4}{(1-x)(1.5-x)(2.5+2x)^2}$$

$$6.2377 = \frac{x^4}{(1-x)(1.5-x)(2.5+2x)^2}$$

$x = 0.98531$ moles

$\xi = 2.5 + 2x = 4.47062$ moles

$y_{H_2} = \dfrac{3x}{2.5+2x} = 0.6612$, $y_{CO_2} = 0.2204$

$y_{CH_3OH} = 0.003286$ $y_{H_2O} = 0.1151$

At the original condition — 10 atm

$$K_p = 2694.687 = \frac{27x^4}{(1-x)(1.5-x)(2.5+2x)^2}(100)$$

or

$$0.998032 = \frac{x^4}{(1-x)(1.5-x)(2.5+2x)^2}$$

$x = 0.9306$ moles

At the lower pressure — 4 atm

$x = 0.9853$ moles

Hence significantly more Hydrogen is produced at the lower pressure. →

Solutions for f(x) = x^4 / ((1-x)(1.5-x)(2.5+2x)^2)
It is a monotonically increasing funtion without multiple roots and 0≤x≤1

| x | f(x) |
|---|---|
| 0.83 | 0.240769785 |
| 0.84 | 0.26983648 |
| 0.844 | 0.282701428 |
| 0.8445 | 0.284364125 |
| 0.845 | 0.286039356 |
| 0.85 | 0.303509652 |
| 0.855 | 0.32238331 |
| 0.8555 | 0.324353661 |
| 0.8556 | 0.324749614 |
| 0.85568 | 0.325066831 |
| 0.856 | 0.326339748 |
| 0.86 | 0.34281585 |
| 0.9 | 0.591400757 |
| 0.93 | 0.986247511 |
| 0.9306 | 0.997845384 |
| 0.95 | 1.529876503 |
| 0.96 | 2.012735202 |
| 0.97 | 2.824384845 |
| 0.98 | 4.458628072 |
| 0.985 | 6.098617388 |
| 0.9853 | 6.232622176 |
| 0.98531 | 6.237183518 |
| 0.9854 | 6.278517507 |
| 0.9855 | 6.32504753 |
| 0.99 | 9.38457424 |