GJ

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ENCH 501: Transport Phenomena Quiz #2 **September 27, 2011**

Time Allowed: 40 mins. **Name:**

Formaldehyde is a base chemical of significant industrial importance. It is used for the production of urea-phenolic and melamine resins that are applied to bind cellulosic materials in the manufacture of clipboard and plywood. It is also used in the manufacture of paints, cosmetics, explosives, fertilizers, dyes, textile and paper.

Formaldehyde (F) is produced from the oxidation of methanol (M) at atmospheric pressures and temperatures of 250 - 400°C. The primary reaction,

1) $CH_3OH + \frac{1}{2}O_2 \rightarrow HCHO + H_2O$

is exothermic. Other reactions also occur and these reduce the yield of formaldehyde. One of these reactions is,

2) $HCHO + 2CH_3OH \rightleftarrows CH_2(OCH_3)_2 + H_2O$

where $CH_2(OCH_3)_2$ is dimethoxymethane (DMM). It is claimed that during the production of formaldehyde from oxidizing methanol, less by-products are formed at higher temperatures.

Supplied with stoichiometric proportions of formaldehyde (1 mole) and methanol (2 moles) in a reactor at 400°C and a pressure of 0.9 atmosphere (as in Calgary), and no products were initially present and no other reactions but that shown in equation 2 occurred, estimate the ***equilibrium composition*** of the compounds in the reactor and the ***error*** associated. Show all your steps.
Is the claim that less by-products are produced justified? Explain.

Data:
The equilibrium constant for the reaction in equation 2, at 500K, is 0.2 atm^{-1}. The heats of formation (kJ/mol), all from the same investigators, are as follows: F, -108.6 ± 0.46 ; M, -74.5 ± 0.4 ; DMM, -348.2 ± 0.79 ; Steam, -241.83 ± 0.04.

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The reaction is:

Heat of formation:	$HCHO$	+	$2CH_3OH$	$\rightleftharpoons$	$CH_2(OCH_3)_2$	+	H_2O
ΔH_f kJ/mol	-108.6 ± 0.46		-74.5 ± 0.4		-348.2 ± 0.79		-241.83 ± 0.04

The data is assumed correlated, as they are all from the same investigators.

The heat of reaction,

$$\Delta H_r = (-348.2 - 241.83) - (-108.6 - 2(74.5))$$

$$= -332.43 \text{ kJ / mole HCHO, \underline{exothermic}}$$

The absolute error in Heat of reaction is:

$$\pm \Delta(\Delta H_r) = 0.46 + 2(0.4) + 0.79 + 0.04$$

$$= 2.09 \text{ kJ/mol}$$

$$\therefore \underset{\text{most probable}}{\Delta H_r} = -332.43 \pm 2.09 \text{ kJ/mol HCHO}$$

To determine the equilibrium composition, apply the van't Hoff equation

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

where $R = 8.314$ kJ/kmol K

and the bounds for ΔH_r are –

lower $\Delta H_r = -334.52$ kJ/mol

upper $\Delta H_r = -330.34$ kJ/mol

At lower limit, for $Kp_1 = 0.2$, $T_1 = 500K$

and $T_2 = 400 + 273.15 = 673.15K$

$$\ln \frac{Kp_2}{0.2} = \frac{-334.52}{8.314(10^{-3})}\left[\frac{1}{500} - \frac{1}{673.15}\right]$$

$$Kp_2 = 2.0488(10^{-10})$$

for the reaction

$$HCHO + 2CH_3OH \rightleftharpoons CH_2(OCH_3)_2 + H_2O$$

t=0 charge, moles	1	2	0	0
at =n, moles	$(1-x)$	$2(1-x)$	x	x

Total = $(3-x)$ moles at equilibrium

The equilibrium constant,

$$Kp = \frac{\bar{P}_{DMM}\,\bar{P}_{H_2O}}{\bar{P}_F\,\bar{P}_M^{\,2}} = \frac{1}{P_t}\left[\frac{x^2}{4(1-x)^3}\right](3-x)$$

given $\bar{P} = y_i P_t$ and $P_t = 0.9$ atm

$$\therefore \quad K_p = \frac{1}{0.9}\left[\frac{x^2(3-x)}{4(1-x)^3}\right]$$

At the lower limit

$$2.0488(10^{-10}) = \frac{1}{3.6}\left(\frac{x^2(3-x)}{(1-x)^3}\right)$$

$$x_L \doteq 1.5680(10^{-5})$$

Estimate K_p at the upper limit

$$\ln \frac{K_{p_2}}{0.2} = \frac{-330.34}{8.314(10^{-3})}\left[\frac{1}{500} - \frac{1}{673.15}\right]$$

$$K_{p_2} = 2.6536(10^{-10})$$

At the upper limit

$$2.6536(10^{-10}) = \frac{1}{3.6}\left(\frac{x^2(3-x)}{(1-x)^3}\right)$$

$$x_u \simeq 1.7845(10^{-5})$$

Combine x_L and x_u

$$x = \left(\frac{x_L + x_u}{2}\right) \pm \frac{(x_u - x_L)}{2}$$

$$= 1.6763(10^{-5}) \pm 1.0825(10^{-6})$$

$\longrightarrow$

At 400 °C, the amount of DMM produced is very small.

Hence the claim that the by-products will be produced only in small amounts is justified

Hint: Solving algebraic eq. for x

To solve for x from

$$2.0488(10^{-10}) = \frac{1}{3.6}\left(\frac{x^2(3-x)}{(1-x)^3}\right)$$

assume $x \ll 1$ $\therefore$ $1-x \simeq 1$

and $3-x \simeq 3$

$$2.0488(10^{-10}) = \frac{1}{3.6}\left(\frac{3x^2}{1}\right)$$

and $x = 1.5680(10^{-5})$

i.e. $x \ll 1$ as assumed and $1-x \triangleq 1$

This is an example of how to solve an equation using approximations.