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ENCH 501: Transport Processes Quiz #2 **September 23, 2003**

Time Allowed: 50 mins. **Name:**

Problem (10 points)

The synthesis of ammonia from elemental hydrogen and nitrogen is a reversible exothermic reaction with an increased yield of ammonia favored at high pressures and low temperatures. The reaction is:

$$3H_2 + N_2 \rightleftharpoons 2NH_3 \qquad \Delta H_r = +100.464\text{kJ}$$

The equilibrium constant for the reaction is defined as:

$$K_p = P_{NH_3} / [\, P_{H_2}{}^{3/2} \; P_{N_2}{}^{1/2}]$$

where P_{NH_3}, P_{H_2} and P_{N_2} are partial pressures. For the reaction, the equilibrium constant is related to pressure **p** (in atm.) and temperature **T** (K) by the *Gillespie equation* (Proc. Nat. Acad. Sci., 1925, **11**, 73) and is given as:

$$\log_{10} K_p = (2172.26 + 1.99082\mathbf{p}) / \mathbf{T} - (5.2405 + 0.002155\mathbf{p})$$

Given that the possible errors in measuring the temperature and the pressure are respectively 25°C and 10 atm., from a stoichiometric feed of pure hydrogen (3 moles) to nitrogen (1 mole) estimate the equilibrium yield of ammonia (i.e. the moles fraction at equilibrium) when the temperature is given as 555°C and the pressure is 250 atm.

Estimate the error for your calculation.

Bonus (2 points)

What are the corresponding yield for ammonia and the error in the result when the pressure equals 400atm. and the temperature is 450°C? Comment.

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Given $p = 250 \pm 10$ atm

$T = (555 + 273) \pm 25$ K

$= 828 \pm 25$ K.

Estimate Kp from Gillespie equation

	p	T		Kp	From final Results y_{NH_3}
measured	250	828		$2.788 (10^{-3})$	0.16
-p, -T	240	803		$3.487 (10^{-3})$	
-p, +T	240	853	lowest	$2.224 (10^{-3})$	0.1314
+p, -T	260	803	highest	$3.54 (10^{-3})$	0.184
+p, +T	260	853		$2.252 (10^{-3})$	

The highest and lowest Kp values are not for both p and T deviations being −ve or +ve. Other p, T combinations are intermediate. Use the extreme values to estimate the error.

The reaction is:

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

	$3H_2$	N_2	$2NH_3$
Supply	3 moles	1 mole	0
At eqm	$3(1-x)$	$(1-x)$	$2x$

for every x moles of nitrogen consumed.

$\therefore$ Total number of moles $= 4 - 2x$

The mole fractions

$NH_3 = x/(2-x) = y_{NH_3}$

$N_2 = \dfrac{1-x}{2(2-x)} = y_{N_2}$

$H_2 = \dfrac{3(1-x)}{2(2-x)} = y_{H_2}$

$$K_p = \frac{P_{NH_3}}{P_{H_2}^{3/2}\, P_{N_2}^{1/2}} = \frac{y_{NH_3}}{y_{H_2}^{3/2}\, y_{N_2}^{1/2}} \cdot \frac{1}{P}$$

For the yield at $P = 250$ atm, $T = 828$ K

$$\frac{x/(2-x)}{\left[\frac{3(1-x)}{2(2-x)}\right]^{3/2}\left[\frac{1-x}{2(2-x)}\right]^{1/2}} \frac{1}{250} = 2.788(10^{-3})$$

or $x = 0.2757$ moles $\therefore y_{NH_3} = \frac{x}{2-x} = 0.15989$

That is, there would be 16 mole % NH_3 in the equilibrium mixture.

When $P = 240$ atm, $T = 853$ K

$x = 0.2323$ moles or $y_{NH_3} = 0.1314$

There would be 13.14 mole % NH_3

When $P = 260$ atm, $T = 803$ K

$x = 0.3250$ moles or $y_{NH_3} = 0.19403$

There would be 19.4 mole % NH_3

We compare the last 2 values with what we expect.

$0.15989 - 0.1314 = 0.02849$
$0.19403 - 0.15989 = 0.03414$

$\therefore$ Higher deviation $= 0.03414 =$ Error

$\therefore y = 0.16 \pm 0.034$

Expected yield

Bonus $P = 400\,atm$ $T = 450°C = 723K$.

		P, atm	T, K	K_p	
		400	723	0.010079	
-P	-T	390	698	0.013916	
-P	+T	390	748	0.007263	lowest
+P	-T	410	698	0.01437	highest
+P	+T	410	748	0.007435	

The pattern is similar to the earlier calculation, but K_p values are larger — as might be expected.

Similar to previous: –

P atm	K_p	x moles	y_{NH_3}
400	$1.0079(10^{-2})$	0.599	0.4276
390	$7.263(10^{-3})$	0.537	0.367
410	$1.437(10^{-2})$	0.66	0.4925

(differences: 0.0605, 0.0649)

The deviation between the higher value and observed is larger.

$\therefore \quad y_{NH_3} = 0.4276 \pm 0.0649$

One expects ~ 42% yeild by increasing P and lowering T.