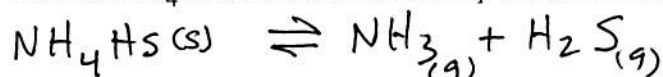


# The ULTIMATE Equilibrium Problem...

Consider the following equation:  $\text{NH}_4\text{HS (s)} \rightleftharpoons \text{NH}_3 \text{ (g)} + \text{H}_2\text{S (g)}$

1. Some solid  $\text{NH}_4\text{HS}$  is placed in an evacuated vessel at  $25^\circ\text{C}$ . After Eq. is attained, the total pressure in the system is 0.659 atm. Some solid  $\text{NH}_4\text{HS}$  remains in the vessel at Eq. CALCULATE  $K_p$ .



$$P_T = 0.659 \text{ atm}$$

$$K_c = [\text{H}_2\text{S}][\text{NH}_3]$$

Solid not in eq expression

$$0.659 = x + x \text{ (equal coefficients)}$$

$$.659 \text{ atm} = 2x \quad x = \frac{0.659}{2} = 0.3295 \text{ atm} \quad \text{So, } K_c = \frac{.330^2}{.330} = .330$$

2. Some extra  $\text{NH}_3 \text{ (g)}$  is injected into the vessel. When Eq. is reestablished, the partial pressure of  $\text{NH}_3 \text{ (g)}$  in the vessel is 2x the partial pressure of  $\text{H}_2\text{S (g)}$ . Calculate the  $P_{\text{NH}_3}$  and  $P_{\text{H}_2\text{S}}$ .

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}}$$

$$\sqrt{x^2} = x = 0.233$$

$$.109 = 2x \cdot x$$

$$\frac{.109}{2} = x^2$$

$$x^2 = .0545$$

$$P_{\text{NH}_3} = 2x = 2(.233) = .466 \text{ atm}$$

$$P_{\text{H}_2\text{S}} = x = .233 \text{ atm}$$

3. In a different experiment,  $\text{NH}_3$  and  $\text{H}_2\text{S}$  are introduced into an evacuated 1.00 L vessel at  $25^\circ\text{C}$ . The initial pressure of each gas is 0.500 atm. Calculate the partial pressure of  $\text{NH}_3 \text{ (g)}$  and  $\text{H}_2\text{S (g)}$  as well as the moles of solid of  $\text{NH}_4\text{HS}$  all present at Eq.

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} = .109$$

$\text{NH}_4\text{HS}$	$\rightarrow$	$\text{NH}_3$	$\text{H}_2\text{S}$
0		.500	.500
+x		-x	-x
x		.500-x	.500-x

$$.109 = (.5 - x)^2$$

$$\sqrt{.109} = .5 - x$$

$$.329 = .5 - x$$

$$x = 0.170$$

$$P_{\text{NH}_3} = .500 - .170 = .330$$

$$P_{\text{H}_2\text{S}} = .500 - .170 = .330$$

$$P_V = nRT \quad n = \frac{PV}{RT}$$

$$n = \frac{.170(1.00\text{L})}{.0821(298)} = .00699 \text{ moles}$$

4. Knowing the  $K_p$  from above, calculate  $K'_p$  for the following reaction:  $2 \text{NH}_3 \text{ (g)} + 2 \text{H}_2\text{S (g)} \rightleftharpoons 2 \text{NH}_4\text{HS (s)}$

Reverse the Rxn and multiply coefficient x 2.

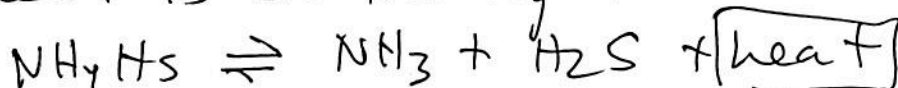
$$\text{If } K_p = .109 \text{ then } K'_p = \frac{1}{(K_p)^2} = \frac{1}{(.109)^2} = 84.2$$

5. If  $K_p$  at  $45^\circ\text{C}$  is 0.00108, is this reaction ENDO- or EXO- ???

$$@ 25^\circ\text{C } K_p = .109 \quad @ 45^\circ\text{C } K_p = .00108$$

this causes a shift towards the left.

Exothermic! So heat is on the right.



6. Considering the original reaction:  $\text{NH}_4\text{HS (s)} \rightleftharpoons \text{NH}_3 \text{ (g)} + \text{H}_2\text{S (g)} + \text{heat}$

- Which way would the reaction shift in each case?
- What would happen to the moles of  $\text{H}_2\text{S}$ ?
- What would happen to  $K$ ?

EXPLAIN your answers....use Energy diagrams and symbols as much as possible!

a. Add more  $\text{NH}_4\text{HS}$ .

No effect. Not in Eq expression!  
 $K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}}$

b. Increase the P by decreasing the volume.

only affects products (gas)  $Q > K$ , shift left, no  $\Delta$  in  $K$

c. Add a catalyst.

reach Eq quickly / no shift, no  $\Delta$  in  $K$ .

d. While maintaining the same volume, add some Argon.

no  $\Delta$  in  $K$ ,  $\text{H}_2\text{S}$  or  $K$ ! or see it as heating up (shift left)

e. While maintaining the same pressure, add some Argon.

Volume would increase  $\rightarrow \downarrow P_{\text{NH}_3} \text{ \& } P_{\text{H}_2\text{S}}$ .

f. Decrease the temperature.

Shift RT.  $\uparrow \text{H}_2\text{S}$ , ~~no  $\Delta$  in  $K$~~

$Q < K$ .

Shift RT

g. Add some HCl.

$\uparrow \text{H}_2\text{S}$ , no  $\Delta$  in  $K$

$K$  will increase



it essentially removes  $\text{NH}_3$

Shift RT,  $\uparrow \text{H}_2\text{S}$ , no  $\Delta$  in  $K$ .

could also get not