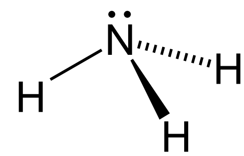
CHEM1032 Cumulative Review (So Far!)

We've covered so much ground since January! This week is a good time to practice some of the concepts and problems we've worked on this semester. (You should get out your plastic-covered equation sheet for these problems.)

Nitrogen is an essential element, necessary for every molecule of protein and DNA and many others. Your body can't directly use N_2, the most common form of nitrogen. Instead, you need "fixed nitrogen." Ammonia (NH_3) is a very important molecule because it provides "fixed nitrogen" to support life.



One way we produce NH_3 industrially for fertilizer is by using the Haber-Bosch process:

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

About 2% of the world's annual energy consumption goes into this process.

Here are some data about NH_3:

$\Delta G_f° = -16.6$ kJ/mol
$\Delta H_f° = -45.9$ kJ/mol
$S° = 192.77$ J/mol·K
normal boiling point is -33.4 °C
C_p (NH_3 gas) = 37.0 J/mol·°C
C_p (NH_3 liquid) = 80.8 J/mol·°C
$\Delta H_{vap}° = 23.25$ kJ/mol (at the normal boiling point)
pK_b is 4.74 so pK_a for NH_4^+ as an acid = 14 − 4.74 = 9.26

molar mass: 17.031 g/mol

$\Delta G_f°$ and $\Delta H_f°$ for $H_2(g)$ and $N_2(g)$ all = 0 kJ/mol (elements in their most stable states)

<u>Phase changes</u>

What is the stable state of matter of NH_3 at 25 °C?

It's a gas.
(Data tells us it boils at −33.4°C)

How much total heat would it take to convert 100.0 g of NH_3 from -50.0 °C to + 50.0 °C?

$100.0\,g\left(\frac{1\text{ mole}}{17.031\,g}\right) = 5.872$ moles of NH_3

heat liquid from −50°C → −33.4°C ($\Delta T = 16.6°C$)

$q = nC\Delta T = (5.872\text{ moles})(80.8\,J/mol°C)(16.6°C) = 7876\,J = 7.876\,kJ$

boil at −33.4°C

$q = 5.872\text{ moles}\,(23.25\,kJ/mol) = 136.52\,kJ$

heat gas from −33.4°C → 50°C ($\Delta T = 83.4°C$)

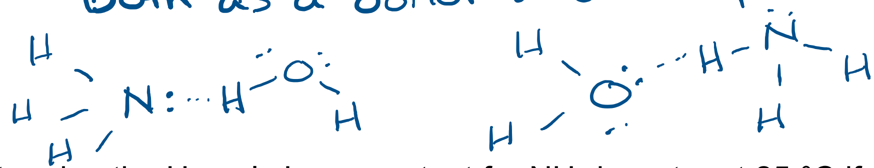
$q = nC\Delta T = (5.872\text{ moles})(37.0\,J/mol°C)(83.4°C) = 18.12\,kJ$

total = 7.88 kJ + 136.52 kJ + 18.12 kJ = $\boxed{162.52\,kJ}$

Solubility

Do you think NH_3 would be very soluble in water? What intermolecular forces would favor solubility? Support your answer with drawings.

yes! NH_3 should be able to hydrogen bond with water both as a donor and acceptor



both O and N are very electronegative

Determine the Henry's Law constant for NH_3 in water at 25 °C if an NH_3 pressure of 0.0220 atm produces a solution with a concentration of 1.30 M. (For this question, you can ignore any reactions between NH_3 and water...but you can also think about whether they will make a big difference to the value you calculate.)

$C = k_H \cdot P$

$1.30\ M = k_H \cdot 0.0220\ atm$

$k_H = 59.1\ M \cdot atm^{-1}$

note that NH_3 will react with water

$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$

but we'll get to that later!

Equilibrium

Think for a second about whether you'd expect the value of $\Delta S_{rxn}°$ for the Haber-Bosch process to be positive or negative. Calculate the actual value of $\Delta S_{rxn}°$ at 25 °C.

I predict negative because 4 moles gas $\rightarrow$ 2 moles gas

$\Delta G°_{rxn} = 2\text{ moles } NH_3(-16.6\ kJ/mol) - \left[2\text{ moles } N_2\left(0\ \frac{kJ}{mol}\right) + 3\text{ moles } H_2\left(0\ \frac{kJ}{mol}\right)\right]$

$= -33.2\ kJ$

$\Delta H°_{rxn} = 2\text{ moles } NH_3(-45.9\ kJ/mol) - \left[1\text{ mole } N_2\left(0\ \frac{kJ}{mol}\right) + 3\text{ moles } H_2\left(0\ \frac{kJ}{mol}\right)\right]$

$= -91.8\ kJ$

$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$

$-33.2\ kJ = -91.8\ kJ - (298.15\ K)\Delta S_{rxn}$

$\boxed{\Delta S_{rxn} = -197\ J/K}$

At equilibrium at some temperature, the concentrations of NH_3, H_2, and N_2 are 1.8×10^{-2}, 3.0×10^{-2}, and 1.5×10^{-2} M respectively. Calculate the equilibrium constant (K_c) for the formation of NH_3 at that temperature.

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(1.8\times10^{-2})^2}{(1.5\times10^{-2})(3.0\times10^{-2})^3} = 800$$

If you were to add 0.8×10^{-2} M N_2 to the reaction above, would the resulting value of ΔG at that moment be positive, negative, or zero? Set up the ICE table and the equilibrium expression that you'd make to determine what the new equilibrium concentration of NH_3 would be. The math gets ugly, so you don't have to solve it all the way through.

you're adding a reactant, so we expect the reaction to shift right, towards products... that would be consistent with a negative ΔG

	N_2 +	$3H_2$ $\rightleftarrows$	$2NH_3$
I	2.3×10^{-2}	3.0×10^{-2}	1.8×10^{-2}
C	$-x$	$-3x$	$+2x$
E	$2.3 \times 10^{-2} - x$	$3.0 \times 10^{-2} - 3x$	$1.8 \times 10^{-2} + 2x$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(1.8 \times 10^{-2} + 2x)^2}{(2.3 \times 10^{-2} - x)(3.0 \times 10^{-2} - 3x)^3} = 800$$

and you can't neglect x because K is too big!

Calculate K for the Haber-Bosch reaction at 25 °C.

$\Delta G_{rxn} = -33.2 \text{ kJ/mol}$ (see above)

$\Delta G = -RT \ln K$

$-33200 \text{ J/mol} = -8.3145 \text{ J/mol}\cdot\text{K} (298.15 \text{ K}) \ln K$

$\ln K = 13.39$

$K = e^{13.39} = 6.55 \times 10^5$

If you were in charge of the chemical plant making NH_3, would it be a good suggestion to improve the production of NH_3 by decreasing the volume (and thus increasing the pressure) of the reaction? Why or why not?

yes! that change would favor the side with fewer moles of gas, which for this reaction is the products side

If you were in charge of the chemical plant making NH_3, would it be a good suggestion to improve the production of NH_3 by heating up the reaction? Why or why not?

no! this reaction is exothermic (ΔH is negative) so you can think of heat as a product... heating it up will shift the reaction back towards reactants

<u>Acid-base chemistry</u>

NH_3 is a base. Draw an example of NH_3 behaving as a Brønsted base. ← proton acceptor

from water: $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

Draw an example of NH_3 behaving as a Lewis base. ← electron pair donor

example above still works!

$\left[H:N\begin{smallmatrix}-H\\-H\\|\\H\end{smallmatrix}\right]^+$ or $F_3B:NH_3$ or $M^{n+}:NH_3$

Write the chemical equation for the reaction quantitated by the K_b for NH_3 and give the value of the K_b.

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 10^{-4.74} = 1.82 \times 10^{-5}$$

Sketch the general shape (no numbers necessary!) of the acid-base titration of NH_3 (weak base) with HBr (strong acid). Would the pH at the equivalence point be greater than, less than, or equal to 7? What would be the pH range where a NH_3/NH_4^+ buffer system would do a good job of buffering pH?