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Advanced Physical Chemistry Problems (VIII), Chemical Equilibrium

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Problems for the Advanced Physical Chemistry Student
Part 8, Chemical Equilibrium

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I. SYNOPSIS

This is a set of problems that were used near the turn of the century and which will be lost when the web site they were on disappears with my demise. Because these problems are being taken from the web and are being edited, their statements and the hints/answers offered are subject to the typical editorial errors that ensue when such work is undertaken in the vacuum of a non-teaching situation. Therefore, I claim any errors for myself, and hate to note that there most likely is no point in contacting me about them for obvious reasons.

II. GIBBS AND HELMHOLTZ FREE ENERGIES

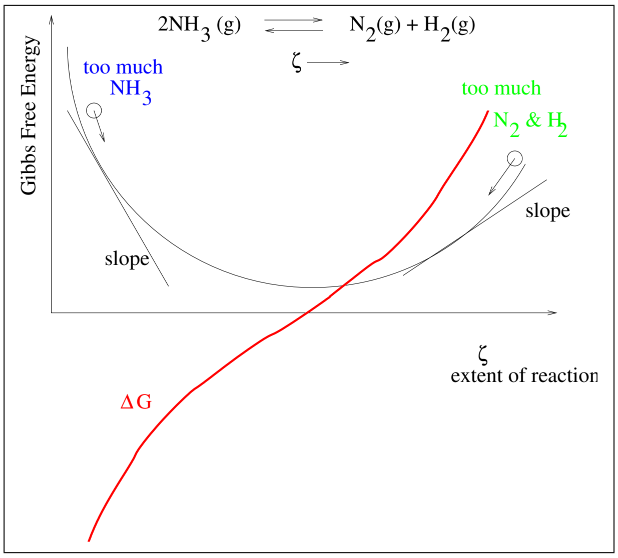

FIG. 1: G and Δ G versus extent of reaction (ζ), seeking equilibrium

1. Define 'ζ' as the fraction of SbCl which reacts. At 238^{o}C and 1.23 atm pressure, $\zeta = 0.718$ for the reaction:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

starting with pure $SbCl_5$. Calculate K_p for this reaction.

Answer and/or Hint

We need to remember how to form the tableau which allows us to understand how the stoichiometry of the situation effects the equilibrium. We have

moles	$SbCl_5$	$SbCl_3$	Cl_2
start	1	0	0
change	$-\zeta$	ζ	ζ
equilibrium	$1-\zeta$	ζ	ζ

where we start with the assumption of one mole of $SbCl_5$ at the outset. At equilibrium, we have $1-\zeta+\zeta+\zeta$ moles of gas, so the mole fractions of the three components at chemical equilibrium are

moles	$SbCl_5$	$SbCl_3$	Cl_2
start	1	0	0
change	$-\zeta$	ζ	ζ
equilibrium	$1-\zeta$	ζ	ζ
ζ_i at eq	$\frac{1-\zeta}{1+\zeta}$	$\frac{\zeta}{1+\zeta}$	$\frac{\zeta}{1+\zeta}$

The partial pressures of the components are then related through Dalton's Law to the mole fractions, and we have

$$K_p = \frac{\left(\frac{\zeta}{1+\zeta}\times 1.23\right)\times 1.23\left(\frac{\zeta}{1+\zeta}\times 1.23\right)\times 1.23}{\left(\frac{1-\zeta}{1+\zeta}\times 1.23\right)\times 1.23}$$

where ζ is 0.718.

2. At 2185^{o}C and 1 atm pressure H_2O(g) is 1.18% decomposed into H_2(g) and $O_($g), i.e.,
$2H_2O$(g)⇌ 2 H_2(g) + O_2(g)
Calculate K_p for the process.

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Answer and/or Hint

This is the same problem as above, except the stoichiometry differs slightly.

3. For the reaction
$2NO_2(g) \rightleftharpoons 2\ NO(g) + O_2(g)$
at 184^{o}C, $K_p = 6.76 \times 10^{-5}$ for a pressure in atm. What is the degree of dissociation of the $NO_2(g)$ at a total pressure of 1 atm?

Answer and/or Hint

This is the reverse of the first two problems, again with different stoichiometry.

4. At 400^{o}K and 1 atm pressure, ΔG^o for the reaction
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
is 850 cal. Calculate the percent decomposition of $PCl_5(g)$ if we started with one mole of $PCl_5(g)$ and no $PCl_3(g)$ or $Cl_2(g)$ in the mixture.

Answer and/or Hint

Here, we need to obtain K_p first before we start the equilibrium tableau computation. We know that

$$K_p = e^{\frac{-\Delta G^o}{RT}}$$

where ΔG^o and R have to be in commensurate units. The rest is straightforward.

5. At 400^{o}K and 1 atm pressure, ΔG^o for the reaction
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
is 850 cal. Calculate the percent decomposition of $PCl_5(g)$ if we started with one mole of $PCl_5(g)$ and one mole of $PCl_3(g)$ and one mole of $Cl_2(g)$ in the mixture.

Answer and/or Hint

This is getting silly.

6. At 250^{o}K and 1 atm pressure, $K_p = 1.78 atm$ for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
Calculate the density of the equilibrium mixture, assuming one starts with one mole of pure $PCl_5(g)$.

Answer and/or Hint

The wrinkle here is to obtain the total mass of the three gases, and use this datum with the volume to obtain the final density.

7. $NH_4HS(s)$ dissociates according to the equation:
$NH_4HS(s) \rightleftharpoons NH_3\ (g) + H_2S(g)$
At a certain temperature, the dissociation pressure of the pure solid is 50 mm Hg. This represents the total pressure when $NH_4HS(s)$ is in equilibrium with equal amounts (by stoichiometry) of ammonia and hydrogen sulfide. If to a flask originally filled with ammonia to a pressure of 41 mm Hg. one adds solid NH_4HS, what will the final pressure be at equilibrium?

Answer and/or Hint

Here, we need to keep in mind that the solid (as long as its present) adds nothing to pressures of the gases involved in the K_p.

The tableau for the equilibrium computation will be approximately:

Pressures	NH_3	H_2S
start	41	0
change	$+\zeta$	ζ
equilibrium	$41+\zeta$	ζ

8. Solid $NH_2CO_2NH_4(s)$ is introduced into at flask containing $NH_3(g)$ at a partial pressure of 200 mm Hg. The temperature is 30^{o}C. K_p for the decomposition of solid:
$NH_2CO_2NH_4\ (s) \rightleftharpoons CO_2\ (g) + 2\ NH_3(g)$
is 291000 in (mm Hg)^3. Calculate the total pressure at equilibrium. (NOTE, this may involve solving a cubic for the 'real' root).

Answer and/or Hint

Pressures	CO_2	NH_3
start	0	200
change	$+p$	$2p$
equilibrium	p	$200+2p$

We then have

$$K_p = 291000 = p \times (p+200)^2$$

The solution of this equation for p results in a value for the partial pressure of the ammonia. The total pressure will be

$$p_{total} = 200 + 2p$$

9. For the reaction:
$H_2S(g) + I_2(s) \rightleftharpoons 2HI(g) + S(s,rhombic)$
K_p is 1.33×10^{-5} atm at 60^oC. What will be the mole fraction of HI in the vapor at this temperature when the total pressure is 1 atm?

Answer and/or Hint

We have

$$K_p = \frac{p_{\mathrm{HI}}^2}{p_{\mathrm{H_2S}}}$$

and if t is defined as the mole fraction of HI then this expression becomes

$$K_p = \frac{(tp_{total})^2}{(1-t)p_{total}}$$

The problem states the total pressure (1 atm), so we have, in essence, an equation for t.

III. EPILOGUE 1

These problems are a review of freshman chemistry problems, and should not be thought of as particularly advanced. However, I've noticed over the years that even if one passes freshman chemistry (even with an "A") these problems are not fully mastered, and the ability to do them diminishes with time.

The re-acquaintance with them after some years, adds zest to the re-learning process.

Just make sure that you understand that the triumph of classical thermodynamics is contained in the equation

$$\Delta G = \Delta G^o + RT\ell n Q_p$$

(for gases). Once full understanding of this is in place, the extensions to liquids, solids, solutions (liquid and solid) etc., are worth the effort, depending on need.

IV. EPILOGUE (STD)

After editing this material for weeks, and continuously finding errors, some small, some huge, I have to wrap it up and send this off. If, in the years 2008-2010 or so, you come across an error, and you e-mail me, I will try to have it corrected.

But since this material is written in LaTeX there is some doubt whether or not I'll have access to a Linux machine, and access to the digitialcommons site. You can try; we'll see what happens, if anything. Thanks to all the students over the last 45 years who've taught me Physical Chemistry.