Question: If the reaction: $A_{(g)} \leftrightarrow 2\, B_{(g)}$ has a $\Delta G° = 0$ J, what is ΔG, K, and the extent of the reaction at equilibrium if $T = 298K$ and $P = 1$ bar?

Answer: First, at equilibrium $\Delta G = 0$ J by definition.

Now we calculate K from $\Delta G = \Delta G° + RT \cdot \ln(K)$, where all the G's are 0 J:

0 J $= 0$ J $+ RT \cdot \ln(K)$ or $\exp(0$ J $/RT) = K$, making $K = 1$ (no units).

Now for the extent of the reaction: First make a table according to the reaction as so:

	A	B
Amount at equilibrium	$n - n \cdot \alpha$	$2n \cdot \alpha$
Mole fractions	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressures	$\dfrac{1-\alpha}{1+\alpha} \cdot P$	$\dfrac{2\alpha}{1+\alpha} \cdot P$

where α (the extent of the reaction) represents the loss of A. Note the total number of moles, regardless of the extent of the reaction, is $n - n \cdot \alpha + 2\alpha \cdot n = n + n \cdot \alpha$. This makes the mole fraction for A $= \dfrac{(1-\alpha)n}{(1+\alpha)n} = \dfrac{1-\alpha}{1+\alpha}$; the mole fraction of B is found in a similar manner. The partial pressures are then the mole fractions times the total pressure P.

Now at equilibrium $K = \displaystyle\prod_i \left(\dfrac{P_i}{P°} \right)^{\upsilon_i}$ where P_i is the partial pressure of species i. As usual, $P°$ is just 1 bar.

K is now: $\dfrac{\left(\dfrac{2\alpha}{1+\alpha} \cdot \dfrac{P}{P°} \right)^2}{\left(\dfrac{1-\alpha}{1+\alpha} \cdot \dfrac{P}{P°} \right)}$

Simplification gives: $K = \left(\dfrac{2\alpha}{1+\alpha} \cdot \dfrac{P}{P°} \right)^2 \left(\dfrac{1+\alpha}{1-\alpha} \cdot \dfrac{P°}{P} \right) = \dfrac{4\alpha^2}{(1+\alpha)(1-\alpha)} \left(\dfrac{P}{P°} \right)$

The neat trick is that since the pure partial pressures and total pressures are all 1 bar, all the pressures disappear:

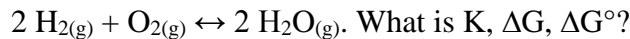$K = \dfrac{4\alpha^2}{(1+\alpha)(1-\alpha)}$

Now since K=1, all we have to do is solve for α:

$\dfrac{4\alpha^2}{(1+\alpha)(1-\alpha)} = \dfrac{4\alpha^2}{1-\alpha^2} = 1$

Therefore: $1-\alpha^2 = 4\alpha^2$ or $1 = 5\alpha^2$, which makes $\alpha = 0.447$ or 44.7 %. Try this yourself: if the reaction was $A_{(g)} \leftrightarrow B_{(g)}$, then you would have calculated $\alpha = 0.5$.

**Question:** At 1 bar of pressure and at 2233 K, water has dissociated by 0.0343 % at equilibrium via:

$2\ H_{2(g)} + O_{2(g)} \leftrightarrow 2\ H_2O_{(g)}$. What is K, ΔG, $\Delta G°$?

What is ΔG, K, and $\Delta G°$ for this reaction at equilibrium? Hint: since water has dissociated so little, then the percent retained of the 2 moles of water is: (100% - 0.0343 %) = 99.9657 %

Answer: First, at equilibrium $\Delta G = 0$ J by definition.

Now first we calculate K and then $\Delta G°$.

If you calculated everything according to the formula:

$2\ H_{2(g)} + O_{2(g)} \leftrightarrow 2\ H_2O_{(g)}$.
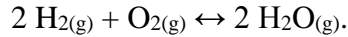
First, make a table expressing changes in mass:

	H_2	O_2	H_2O
Amount at equilibrium	$2n - 2n\cdot\alpha$	$n - \alpha\cdot n$	$2n\cdot\alpha$
Mole fractions	$\dfrac{2-2\alpha}{3-\alpha}$	$\dfrac{1-\alpha}{3-\alpha}$	$\dfrac{2\alpha}{3-\alpha}$
Partial pressures	$\dfrac{2-2\alpha}{3-\alpha}\cdot P$	$\dfrac{1-\alpha}{3-\alpha}\cdot P$	$\dfrac{2\alpha}{3-\alpha}\cdot P$

where α represents the loss of water. Note the total number of moles, regardless of the extent of the reaction, is $2n-2n\cdot\alpha + n-\alpha\cdot n + 2\alpha\cdot n = 3n - n\cdot\alpha$. This makes the mole fraction for water = $\dfrac{2n\alpha}{(3-\alpha)n} = \dfrac{2\alpha}{3-\alpha}$; the other mole fractions are found in a similar manner. The partial pressures are then the mole fractions times the total pressure P.

Now at equilibrium $K = \prod\limits_i \left(\dfrac{P_i}{P°}\right)^{\upsilon_i}$ where P_i is the partial pressure of species i. As usual, $P°$ is just 1 bar.

K is now: $\dfrac{\left(\dfrac{2\alpha}{3-\alpha}\cdot\dfrac{P}{P°}\right)^2}{\left(\dfrac{2-2\alpha}{3-\alpha}\cdot\dfrac{P}{P°}\right)^2\cdot\left(\dfrac{1-\alpha}{3-\alpha}\cdot\dfrac{P}{P°}\right)}$

Simplification gives: $K = \left(\dfrac{2\alpha}{3-\alpha}\cdot\dfrac{P}{P°}\right)^2\left(\dfrac{3-\alpha}{2-2\alpha}\cdot\dfrac{P°}{P}\right)^2\left(\dfrac{3-\alpha}{1-\alpha}\cdot\dfrac{P°}{P}\right) = \dfrac{4\alpha^2(3-\alpha)}{(1-\alpha)(2-2\alpha)^2}\left(\dfrac{P°}{P}\right)^2$

The neat trick is that since the pure partial pressures and total pressures are all 1 bar, all the pressures disappear:

$K = \dfrac{4\alpha^2(3-\alpha)}{(1-\alpha)(2-2\alpha)^2}$

Now since the reaction has gone to 0.0343 % completion, then $\alpha = 0.999657$ (note how this makes the number of moles of water close to 2 moles, which makes sense), you find :
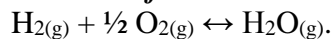
$K = 4.9536\times10^{10}$.

Last is $\Delta G°$, due to the relationship $\Delta G = \Delta G° + RT\cdot\ln(K)$, we know that:

$\Delta G° = -RT\cdot\ln(K) = -8.314$ J/K/mol $\times 2233$ K $\times \ln(4.9536\times10^{10}) = -4.572\times10^5$ J/mol = -457.2 kJ/mol.

Note a neat little fact- this reaction represents *forming two moles* of gas-phase water from its elements. If I look up $\Delta G°$ from the table, I see it is -228.6 kJ/mol, which represents the Gibb's energy to form one mole of gas phase water. Thus forming two moles would be:
$2 \times$ -228.6 kJ/mol = -457.2 kJ/mol, the same number!

Note that if I had written the equation:
$H_{2(g)} + ½ O_{2(g)} \leftrightarrow H_2O_{(g)}$.
Then the table would have looked like:

	H_2	O_2	H_2O
Amount at equilibrium	$n - n·\alpha$	$½ (n - \alpha·n)$	$n·\alpha$
Mole fractions	$\dfrac{1-\alpha}{1.5-0.5\alpha}$	$\dfrac{0.5-0.5\alpha}{1.5-0.5\alpha}$	$\dfrac{\alpha}{1.5-0.5\alpha}$
Partial pressures	$\dfrac{1-\alpha}{1.5-0.5\alpha}·P$	$\dfrac{0.5-0.5\alpha}{1.5-0.5\alpha}·P$	$\dfrac{\alpha}{1.5-0.5\alpha}·P$

Do the algebra, and you will see that:

K is now: $\dfrac{\left(\dfrac{\alpha}{1.5-0.5\alpha}·\dfrac{P}{P°}\right)}{\left(\dfrac{0.5-0.5\alpha}{1.5-0.5\alpha}·\dfrac{P}{P°}\right)^{½}·\left(\dfrac{1-\alpha}{1.5-0.5\alpha}·\dfrac{P}{P°}\right)}$

Simplification gives: $K = \left(\dfrac{\alpha}{1.5-0.5\alpha}·\dfrac{P}{P°}\right)\left(\dfrac{1.5-0.5\alpha}{0.5-0.5\alpha}·\dfrac{P°}{P}\right)^{½}\left(\dfrac{1.5-0.5\alpha}{1-\alpha}·\dfrac{P°}{P}\right) = \dfrac{\sqrt{2}·\alpha(1.5-0.5\alpha)^{½}}{(1-\alpha)(1-\alpha)^{½}}$

Now when you plug in $\alpha = 0.999657$ as before, you find K = 2.2257×10^5.
Last: $\Delta G° = $ -RT·ln(K) = -8.314 J/K/mol $\times$ 2233 K $\times$ ln(2.2257×10^5) = -2.286×10^5 J/mol = -228.6 kJ/mol, which is the same as $\Delta G°$ from the table for *forming 1 mole* of water vapor.

Question: I looked up that $\Delta G°$ is -23.0 kJ/mol for the following reaction:

$ClNO_2(g) + NO(g) \leftrightarrow NO_2(g) + ClNO(g)$
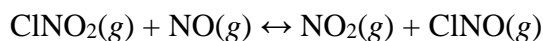
How much has this reaction proceeded if you start with n moles of both reactants, assuming the pressure is 1 bar and let's say temperature is 25 °C?

Here is a hint: starting with the normal table:

	ClNO$_2$	NO	NO$_2$	ClNO
Amount at equilibrium	n·(1-α)	n·(1-α)	n·α	n·α
Mole fractions	$\dfrac{n\cdot(1-\alpha)}{2n}$	$\dfrac{n\cdot(1-\alpha)}{2n}$	$\dfrac{n\cdot\alpha}{2n}$	$\dfrac{n\cdot\alpha}{2n}$
Partial pressures	$\dfrac{(1-\alpha)}{2}\cdot P$	$\dfrac{(1-\alpha)}{2}\cdot P$	$\dfrac{\alpha}{2}\cdot P$	$\dfrac{\alpha}{2}\cdot P$

where α represents the extent of the reaction. Note the total number of moles, regardless of the

extent of the reaction, is 2n. Now at equilibrium K = $\displaystyle\prod_i \frac{P_i^{v_i}}{P^{\circ v_i}}$, where P_i is the partial pressure of

species i. As usual, $P°$ is just 1 bar. K is now: $\dfrac{\left(\dfrac{\alpha}{2}\cdot\dfrac{P}{P°}\right)\cdot\left(\dfrac{\alpha}{2}\cdot\dfrac{P}{P°}\right)}{\left(\dfrac{(1-\alpha)}{2}\cdot\dfrac{P}{P°}\right)\cdot\left(\dfrac{(1-\alpha)}{2}\cdot\dfrac{P}{P°}\right)}$. Simplification gives:

$\left(\dfrac{2}{(1-\alpha)}\cdot\dfrac{P°}{P}\right)\cdot\left(\dfrac{2}{(1-\alpha)}\cdot\dfrac{P°}{P}\right)\cdot\left(\dfrac{\alpha}{2}\cdot\dfrac{P}{P°}\right)\cdot\left(\dfrac{\alpha}{2}\cdot\dfrac{P}{P°}\right)= \left(\dfrac{4}{(1-\alpha)^2}\right)\cdot\left(\dfrac{\alpha^2}{4}\cdot\right)=\dfrac{\alpha^2}{(1-\alpha)^2}=\dfrac{\alpha^2}{1-2\alpha+\alpha^2}$. Now when you

plug this into the expression for the Gibbs energy at equilibrium: $\ln\left(\dfrac{\alpha^2}{1-2\alpha+\alpha^2}\right)=\dfrac{-\Delta G°}{R\cdot T}$, you

can solve for α. Hint hint: if $A\alpha^2+B\alpha+C=0$, then the two possible values of α are:

$\dfrac{-B+\sqrt{B^2-4AC}}{2A}$ or $\dfrac{-B-\sqrt{B^2-4AC}}{2A}$.

Answer: Starting with: $\ln\left(\dfrac{\alpha^2}{1-2\alpha+\alpha^2}\right)=\dfrac{-\Delta G°}{R\cdot T}$, plug in everything we know:

$\ln\left(\dfrac{\alpha^2}{1-2\alpha+\alpha^2}\right)=-\dfrac{-23,000 J/mol}{8.314 J/K/mol\cdot 298.15K}=9.28$. Next, take the exponential of both sides:

$\left(\dfrac{\alpha^2}{1-2\alpha+\alpha^2}\right)=e^{9.28}=1.07\times10^4$. Next, you have to simplify it:

$\alpha^2 = 1.07\times10^4\cdot\left(1-2\alpha+\alpha^2\right)$ and therefore: $(1-1.07\times10^4)\alpha^2+2\cdot1.07\times10^4\alpha-1.07\times10^4=0$

Use the quadratic equation $\dfrac{-B-\sqrt{B^2-4AC}}{2A}$ makes $\alpha=1.0097$, which is impossible. Therefore the

correct one is $\dfrac{-B+\sqrt{B^2-4AC}}{2A}$, which makes $\alpha= 0.99$.