## PROBLEM SET 5

1) a) Find the equilibrium constant at 298 K for the reaction

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\mathrm{PCI}_{5} \rightarrow \mathrm{PCI}_{3}+\mathrm{CI}_{2(\mathrm{~g})}
$$

b) Find the total pressure if 0.001 mol of $\mathrm{PCI}_{5}$ is placed in a vessel with a volume of 20 L at 298 K and allowed to equilibrate. Assume ideal gas behavior.
2) a) Find $\Delta \mathrm{H}^{0}, \Delta \mathrm{G}^{0}$ and $\mathrm{K}_{\mathrm{p}}$ at 298 K for $\mathrm{I}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{I}_{(\mathrm{g})}$
b) Assume $\Delta \mathrm{H}^{0}$ constant find temperature at which $\mathrm{K}_{\mathrm{p}}=1$
c) Assume $\Delta \mathrm{H}^{0}$ constant find $\mathrm{K}_{\mathrm{p}}$ at 1000 K .
d) Assume $\Delta \mathrm{Cp}$ constant find $\mathrm{K}_{\mathrm{p}}$ at 1000 K .
3) A certain gas mixture held at 395 K has the following initial pressures. $\mathrm{P}\left(\mathrm{Cl}_{2}\right)=351.4$ torr, $\mathrm{P}\left(\mathrm{COCl}_{2}\right)=0$. At equilibrium total pressure is 439.5 torr is held constant. Find K at 395 K for
$\mathrm{CO}+\mathrm{Cl}_{2} \rightarrow \mathrm{COCl}_{2}$
4) For the ideal gas reaction $\mathrm{PCI}_{5} \rightarrow \mathrm{PCI}_{3}+\mathrm{CI}_{2(\mathrm{~g})}$

State whether equilibrium shifts to the right or left when each of the following changes is made in an equilibrium mixture at $25^{\circ} \mathrm{C}$
a) T is decreased at constant P
b) $\quad \mathrm{V}$ is decreased at constant T
c) Some PCl5 is removed at constant T and V
d) $\quad \mathrm{He}_{(\mathrm{g})}$ is added at constant T and V
e) $\quad \mathrm{He}_{(\mathrm{g})}$ is added at constant T and P
5) For $2 \mathrm{CO}(\mathrm{g})+\mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{CO}_{2(\mathrm{~g})}$ assume ideal gas behavior and $\Delta \mathrm{G}^{0}{ }_{298}=-514.382 \mathrm{kj} / \mathrm{mol}$ and $\Delta \mathrm{H}^{\mathrm{o}}{ }_{\mathrm{T}}(\mathrm{kj} / \mathrm{mol})$ $=-565.968+0.0015(\mathrm{~T}-298)+2.85 * 10^{-6}\left(\mathrm{~T}^{2}-298^{2}\right)+1448((1 / \mathrm{T})-(1 / 298))$
Find an expression for $\ln K_{p}(T)$ and calculate $K_{p}$ at 1000 K for this reaction.
6) Suppose 1.0 mol of $\mathrm{CO}_{2}$ and 1.0 mol of $\mathrm{COF}_{2}$ are placed in a very big vessel at $25^{\circ} \mathrm{C}$ and a catalyst for the gas phase reaction $2 \mathrm{COF}_{2} \leftrightarrow \mathrm{CO}_{2}+\mathrm{CF}_{4}$ is added. Find the equilibrium amounts. $\Delta \mathrm{G}^{\mathrm{o}}{ }_{298}=-35 \mathrm{kj} / \mathrm{mol}$
7) For the ideal gas reaction $\mathrm{N}_{2}+3 \mathrm{H}_{2} \leftrightarrow 2 \mathrm{NH}_{3}$ suppose 1 mol of $\mathrm{N}_{2}$ and 3 mol of $\mathrm{H}_{2}$ react at constant $T$ and $P$, no other gases are present initially. Let x be the number of moles of $\mathrm{N}_{2}$ that have reacted when equilibrium is reached. $\left(\mathrm{x}=\varepsilon_{\mathrm{eq}}\right)$
Show that,
$\mathrm{X}=1-[1-\mathrm{s} /(\mathrm{s}+4)]^{1 / 2}, \quad \mathrm{~s}=\left(27 \mathrm{~K}_{\mathrm{p}}\right)^{1 / 2} \mathrm{P} / \mathrm{P}^{*}$
8) Nitrogen trioxide dissociates according to the reaction
$\mathrm{N}_{2} \mathrm{O}_{3(\mathrm{~g})} \leftrightarrow \mathrm{NO}_{2(\mathrm{~g})}+\mathrm{NO}_{(\mathrm{g})}$
When one mole of $\mathrm{N}_{2} \mathrm{O}_{3(\mathrm{~g})}$ is held at $25^{\circ} \mathrm{C}$ and 1 bar total pressure until equilibrium is reached, the extent of reaction is 0.30 . What is $\Delta_{\mathrm{r}} \mathrm{G}^{\circ}$ for this reaction at $25^{\circ} \mathrm{C}$ ?
9) Calculate the molar Gibbs energy of butane isomers for extents of reaction of $0.2,0.4,0.6$ and 0.8 for the reaction n-butane $=$ isobutene at 1000 K and 1 bar.
At $1000 \mathrm{~K} \Delta_{\mathrm{r}} \mathrm{G}^{0}(\mathrm{n}$-butane $)=270 \mathrm{~kJ} / \mathrm{mol}, \quad \Delta_{\mathrm{r}} \mathrm{G}^{0}(\mathrm{n}$-butane $)=276.6 \mathrm{~kJ} / \mathrm{mol}$
Make a plot and show that the minimum corresponds to the equilibrium extent of reaction.
10) At $250{ }^{\circ} \mathrm{C}, \mathrm{PCl}_{5}$ is $80 \%$ dissociated at a pressure of 1.013 bar, and so $\mathrm{K}=1.80$. What is the extent of reaction at equilibrium after sufficient nitrogen has been added at constant pressure to produce a nitrogen partial pressure of 0.9 bar? The total pressure is maintained at 1 bar.

