## Equilibrium Problems (no calculator)

You can do these problems with or without a calculator. The answers here were calculated without a calculator.

1. For the equilibrium
$\mathrm{A}(\mathrm{g}) \rightleftharpoons \mathrm{B}(\mathrm{g})+1 / 2 \mathrm{C}(\mathrm{g})$
$\mathrm{K}_{\mathrm{c}}=4.0 \times 10^{-13}$ at $27^{\circ} \mathrm{C}$.
a) Evaluate $K_{P}$ at $27^{\circ} \mathrm{C} .\left[\mathbf{2 . 0} \times \mathbf{1 0}^{-\mathbf{1 2}}\right]$
b) If a flask initially containing only 1.00 bar of $\mathrm{A}(\mathrm{g})$ is allowed to come to equilibrium, what will be the equilibrium pressure of each species?
$\left[P_{A}=1\right.$ bar; $P_{B}=2.0 \times 10^{-8}$ bar; $P_{C}=1.0 \times 10^{-8}$ bar $]$
2. Bromine and chlorine both dissolve in carbon tetrachloride, whereupon they react (slowly) to form BrCl :
$\mathrm{Br}_{2}\left(\mathrm{CCl}_{4}\right)+\mathrm{Cl}_{2}\left(\mathrm{CCl}_{4}\right) \rightleftharpoons 2 \mathrm{BrCl}\left(\mathrm{CCl}_{4}\right)$

Under equilibrium conditions at some temperature, $\left[\mathrm{Br}_{2}\right]=\left[\mathrm{Cl}_{2}\right]=0.50 \mathrm{M}$, and $[\mathrm{BrCl}]=0.10 \mathrm{M}$.
a) Evaluate the equilibrium constant for this reaction at $25^{\circ} \mathrm{C}$. [ $\mathbf{0 . 0 4 0}$ or $\left.\mathbf{1 / 2 5}\right]$
b) If 0.22 moles of BrCl were added to the equilibrium mixture you found in (a), what would be the new equilibrium concentrations of all species present? Assume 1 L of solution. $\left(\left[\mathrm{Br}_{2}\right]=\left[\mathrm{Cl}_{2}\right]=\mathbf{0 . 6 0} \mathbf{M} ;[\mathrm{BrCl}]=\mathbf{0 . 1 2} \mathbf{M}\right.$ )
3. Predict the effect each of the following would have on the reaction (initially at equilibrium):

$$
\mathrm{CoCl}_{4}^{-2}(\mathrm{aq})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{+2}(\mathrm{aq})+4 \mathrm{Cl}^{-1}(\mathrm{aq}) \quad \Delta \mathrm{H}^{\circ}=-14 \mathrm{~kJ}
$$

Indicate your choice by writing shift $\underline{\text { Right, shift }} \underline{\text { Left, or }} \underline{\mathbf{N} o}$ change:
a) Adding HCl gas
b) Heating the reaction
c) Adding $\mathrm{AgNO}_{3}(\mathrm{AgCl}$ is insoluble)
d) Adding water

## [L L R R]

4. The ionization of water is an equilibrium process for which $\mathrm{K}_{\mathrm{c}}=1.0 \times 10^{-14}$ at $25^{\circ} \mathrm{C}$ :
$\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-1}(\mathrm{aq}) \quad \Delta \mathrm{H}=+57 \mathrm{~kJ}$

Should $\mathrm{K}_{\mathrm{w}}$ be larger or smaller at 75 than at 25 ? How do you know?
Determine the approximate $\mathrm{K}_{\mathrm{w}}$ of water at $75^{\circ} \mathrm{C}$. [about $\mathbf{2} \times \mathbf{1 0}^{-13}$ ]
5. The normal boiling point of a liquid is $67^{\circ} \mathrm{C}$ and its enthalpy of vaporization is $34 \mathrm{~kJ} / \mathrm{mol}$. What is its vapour pressure (in atmospheres) at $27^{\circ} \mathrm{C}$ ? [about 0.2]
6. Solid compound A decomposes according to the endothermic reaction:
$\mathrm{A}(\mathrm{s}) \rightleftharpoons 2 \mathrm{~B}(\mathrm{~g})+\mathrm{C}(\mathrm{g}) \quad \mathrm{K}_{\mathrm{p}}=1.08 \times 10^{-4}$
a) If 50.0 mmol of $\mathrm{A}(\mathrm{s})$ is placed in a $6.10-\mathrm{L}$ sealed, evacuated flask at $25^{\circ} \mathrm{C}$, calculate the total pressure in the flask at equilibrium. ( $9.0 \times \mathbf{1 0}^{-\mathbf{2}} \mathbf{b a r}$ )
b) How many millimoles of $\mathrm{A}(\mathrm{s})$ will be left at equilibrium in the experiment described in part (a)? (42.5)
c) If some $\mathrm{A}(\mathrm{s})$ is placed in a $6.10-\mathrm{L}$ evacuated flask at $25^{\circ} \mathrm{C}$ and some $\mathrm{C}(\mathrm{g})$ added so that the partial pressure of $\mathrm{C}(\mathrm{g})$ at equilibrium is 1.00 bar , calculate the equilibrium partial pressure of $\mathrm{B}(\mathrm{g})$ in the system. (about $\mathbf{1 \times 1 0 ^ { - 2 }}$ bar)
d) What is the value of $K_{p}$ for the equilibrium:
$4 \mathrm{~B}(\mathrm{~g})+2 \mathrm{C}(\mathrm{g}) \rightleftharpoons 2 \mathrm{~A}(\mathrm{~s})$
(about $9 \times 10^{7}$ )
e) If the equilibrium $\mathrm{B}(\mathrm{g}) \rightleftharpoons \mathrm{D}(\mathrm{g})$ has equilibrium constant $\mathrm{K}_{\mathrm{p}}=5.0 \times 10^{-3}$, determine the equilibrium constant for the reaction
$\mathrm{A}(\mathrm{s}) \rightleftharpoons \mathrm{C}(\mathrm{g})+2 \mathrm{D}(\mathrm{g})$
(about $3 \times 10^{-9}$ )
7. The fastest growing use of methanol $\left(\mathrm{CH}_{3} \mathrm{OH}\right)$ is to make the octane enhancer methyl tertbutyl ether. Today all methanol is produced (as a gas) by the reaction of carbon monoxide and hydrogen. The value of $\mathrm{K}_{\mathrm{p}}$ for this reaction is (about) $2.0 \times 10^{-4}$ at $327 .{ }^{\circ} \mathrm{C}$.
a) Write the equilibrium reaction for the production of methanol.
$\left(2 \mathrm{H}_{2}(\mathrm{~g})+\mathbf{C O}(\mathrm{g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})\right)$
b) What is the value of $\mathrm{K}_{\mathrm{c}}$ at $327 .{ }^{\circ} \mathrm{C}$ ? (about 0.5 )
c) In which direction will this reaction shift if the temperature is raised, given that the $\Delta \mathrm{H}^{\circ}{ }_{\mathrm{rxn}}=-90.7 \mathrm{~kJ}$ ? Explain! (shifts to left because heat is a product when rxn. is exothermic, try to use up 'excess" heat to re-establish equilibrium.)
d) In the industrial process, the stoichiometric ratio of CO to $\mathrm{H}_{2}$ is used. If the reaction is carried out at an initial total pressure of 300 . bar, what are the initial partial pressures of CO and $\mathrm{H}_{2}$ ? (100. bar CO, 200. bar $\mathbf{H}_{2}$ )
8. A flask initially contains only NOBr gas. Once heated to a temperature T, $20.0 \%$ of the original gas decomposes via the following equation to give a total pressure of 0.33 bar at equilibrium:
$2 \mathrm{NOBr}(\mathrm{g}) \rightleftharpoons 2 \mathrm{NO}(\mathrm{g})+\mathrm{Br}_{2}(\mathrm{~g})$
a) Determine the original pressure of NOBr in the flask. ( 0.30 bar )
b) What is the value of $K_{p}$ at this temperature $T$ ? $\left(1.9 \times 10^{-\mathbf{3}}\right.$ or $\left.\mathbf{3} / \mathbf{1 6 0 0}\right)$
c) If the value of $\mathrm{K}_{\mathrm{c}}$ at this temperature T is $3.9 \times 10^{-5}$, determine the temperature T . ( 600 K)
9. For the equilibrium:

$$
\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})
$$

At some temperature $\mathrm{T}_{1}, \mathrm{~K}_{\mathrm{p}}=2.25$. An unknown quantity of pure $\mathrm{PCl}_{5}(\mathrm{~g})$ is placed in an evacuated flask and heated to $\mathrm{T}_{1}$. When equilibrium was established, the partial pressure of $\mathrm{PCl}_{5}(\mathrm{~g})$ was found to be 0.25 bar.
a) What were the partial pressures of $\mathrm{PCl}_{3}$ and $\mathrm{Cl}_{2}$ at equilibrium? ( 0.75 bar)
b) Determine the original pressure of $\mathrm{PCl}_{5}$ (before any reaction) and the percent dissociation of $\mathrm{PCl}_{5}$ at equilibrium. ( $\mathbf{1 . 0 0} \mathbf{~ b a r , ~} \mathbf{7 5}$ \%)
c) What is the value of $\mathrm{K}_{\mathrm{c}}$ for the reaction if $\mathrm{T}_{1}$ is $327^{\circ} \mathrm{C}$ ? (about $5 \times \mathbf{1 0}^{-\mathbf{2}}$ )
10. For the following system:

$$
\mathrm{C}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{CO}(\mathrm{~g})
$$

At $700 .{ }^{\circ} \mathrm{C}$ in a 2.00 L flask there are 0.100 moles of $\mathrm{CO}, 0.200$ moles of $\mathrm{CO}_{2}$, and 0.400 moles of C at equilibrium. At $600 .{ }^{\circ} \mathrm{C}$, an additional 0.0400 moles of C forms at equilibrium.
a) The process as written is: exothermic or endothermic
b) Determine the value of $\mathrm{K}_{\mathrm{c}}$ at $600 .{ }^{\circ} \mathrm{C}$ and $700 .{ }^{\circ} \mathrm{C} .\left(\mathbf{K}_{\mathbf{c}}=\mathbf{0 . 0 2 5 0}\right.$ at $700 .{ }^{\circ} \mathrm{C}, \mathbf{8 . 3 \times 1 0} \mathbf{1 - 4}$ at $600 .{ }^{\circ} \mathrm{C}$ )
c) An additional 0.200 moles of C is added to the flask at $600 .{ }^{\circ} \mathrm{C}$. What will be the effect on:

| i) | $\mathrm{K}_{\mathrm{c}}$ | increase | decrease | no effect |
| :--- | :--- | :--- | :--- | :--- |
| ii) | $\mathrm{P}_{\mathrm{CO}}$ | increase | decrease | no effect |
| iii) | $\mathrm{P}_{\mathrm{CO} 2}$ | increase | decrease | no effect |

11. Consider the equilibrium:
$4 \mathrm{NH}_{3}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 4 \mathrm{NO}_{2}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \Delta \mathrm{H}^{\circ}=-1381 \mathrm{~kJ}$
Predict whether the equilibrium number of moles of $\mathrm{NH}_{3}$ will increase or decrease and the direction that the reaction will shift in order to establish a new equilibrium if:
i) the volume of the system is decreased ( $\downarrow$,shifts to right)
ii) the temperature of the system is increased ( $\uparrow$,shifts to left)
iii) some $\mathrm{O}_{2}$ is added to the container ( $\downarrow$,shifts to right)
iv) some He is added to the container (no effect)
v) some $\mathrm{NH}_{3}$ is added to the container ( $\uparrow$, shifts to right)
vi) some $\mathrm{H}_{2} \mathrm{O}$ is removed from the container (no effect as long as some water remains)
12. 0.50 moles of $\mathrm{N}_{2} \mathrm{O}_{4}$ were introduced into a 0.25 L flask. Determine the equilibrium concentrations of $\mathrm{N}_{2} \mathrm{O}_{4}$ and $\mathrm{NO}_{2}$ if $\mathrm{K}_{\mathrm{c}}$ for the equilibrium
$\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}$
is $5.0 \times 10^{-7} .\left(\mathbf{N}_{2} \mathbf{O}_{4}=\mathbf{2 . 0} \mathbf{~ M} ; \mathbf{N O}_{2}=\mathbf{1 . 0} \times \mathbf{1 0}^{-\mathbf{3}} \mathbf{M}\right)$
13. Some antimony sulfide and 500 mmol of $\mathrm{H}_{2}$ were placed in a 500 mL flask and heated.

What were the equilibrium concentrations of $\mathrm{H}_{2}$ and $\mathrm{H}_{2} \mathrm{~S}$ once equilibrium had been reached?
$\mathrm{Sb}_{2} \mathrm{~S}_{3}(\mathrm{~s})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{Sb}(\mathrm{s})+3 \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g}) \quad \mathrm{K}_{\mathrm{c}}=0.216$
$\left(\left[\mathrm{H}_{2}\right]=\mathbf{0 . 6 2 5} \mathrm{M} ;\left[\mathrm{H}_{2} \mathrm{~S}\right]=0.375 \mathrm{M}\right)$
14. 0.100 mol of $\mathrm{H}_{2}$ and 0.100 mol of HI were placed in a 1.00 L container and heated.

Determine the equilibrium concentrations of all species.

$$
\begin{aligned}
& \mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{~g}) \quad \mathrm{K}_{\mathrm{c}}=5.0 \times 10^{9} \\
& \left(\left[\mathbf{H}_{\mathbf{2}}\right]=[\mathbf{H I}]=\mathbf{0 . 1 0 0} \mathbf{M},\left[\mathbf{I}_{\mathbf{2}}\right]=\mathbf{2 . 0} \times \mathbf{1 0}^{-\mathbf{1 1}} \mathbf{M}\right)
\end{aligned}
$$

