Chapter 9

## Chapter 9: Example: expansion work

Calculate the amount of work $(\mathrm{kJ})$ done during a synthesis of ammonia in which the volume contracts from 8.6 Liters (initial) to 4.3 Liters (final) at a constant external pressure of 44 atm .
$\mathrm{w}=-\mathrm{P} \Delta \mathrm{V}=-(44 \mathrm{~atm})^{*}$ (4.3 Liters - 8.6 Liters) wrong units
1 liter atm $=101.33$ Joule $\longleftarrow$ memorize this
(use this slide instead)
$\mathrm{w}=-(44 \mathrm{~atm})^{*}(-4.3$ liters $)=189.2$ liter atm
$\mathrm{w}=189.2$ liter atm * $\frac{101.33 \text { Joule }}{1 \text { liter atm }}=19171.636$ Joule
$w=19171.636$ Joule $\times \frac{1 \mathrm{~kJ}}{1000 \mathrm{~J}}=19 \mathrm{~kJ}$

## Calorimetry and Heat Capacity

$$
q=\mathrm{c} m \Delta T \quad c=\text { specific heat capacity }\left(\mathrm{J} / \mathrm{g}^{\circ} \mathrm{C}\right)
$$

$q=C_{m}$ mole $\Delta T \quad C_{m}=$ molar heat capacity $\mathrm{J} / \mathrm{mol}{ }^{\circ} \mathrm{C}$

Watch units, put equations on to 3 " $\times 5$ ",
get chart with c or $\mathrm{C}_{\mathrm{m}}$ values

## HW 9.5: Hess's Law

Want enthalpy for the following reaction:

$$
\mathrm{CO}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}^{\mathrm{o}}=?
$$

Have the following equations and enthalpies:
(a) $2 \mathrm{CO}(\mathrm{g}) \rightarrow 2 \mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}^{\mathrm{o}}=221.08 \mathrm{~kJ}$
(b) $\mathrm{CO}_{2}(\mathrm{~g}) \rightarrow \mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}^{0}=+393.51 \mathrm{~kJ}$

Use Hess's Law to calculate the enthalpy for the reaction above.
(a) $1 / 2$ of rxn (a)
$\mathrm{CO}(\mathrm{g}) \rightarrow \mathscr{C}(\mathrm{s})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}^{0}=+110.54 \mathrm{~kJ}$
(b) Reverse direction of reaction
$\mathrm{C}(\mathrm{s})+\mathrm{O} / 2(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}^{0}=-393.51 \mathrm{~kJ}$
$\mathrm{CO}(\mathrm{g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}^{\mathrm{o}}=-282.97 \mathrm{~kJ}$

## HW 9.6: Standard Heats of Formation

$$
\left.\Delta H^{\circ}=\Delta H_{\mathrm{f}}^{\circ}(\text { Products })-\Delta H_{\mathrm{f}}^{\circ} \text { (Reactants }\right)
$$

$$
a \mathrm{~A}+b \mathrm{~B} \longrightarrow c \mathrm{C}+d \mathrm{D}
$$


$\Delta H_{\mathrm{f}}^{\circ}[\mathrm{HCl}(\mathrm{g})]=-92.31 \mathrm{~kJ} / \mathrm{mol}$ from chart Appendix B $\left.\Delta H_{\mathrm{f}}^{\mathrm{f}}\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right]=-285.8 \mathrm{~kJ} / \mathrm{mol}\right\}$ from your text

HW 9.6: Standard Heats of Formation - generalized equation $\Delta H^{\circ}=\Delta H_{f}^{\circ}$ (Products) $-\Delta H_{f}^{\circ}$ (Reactants)

$$
\underbrace{\begin{array}{c}
a \mathrm{~A}
\end{array}+b \mathrm{~B} \longrightarrow c \mathrm{C}+d \mathrm{D}}_{\text {Reactants }} \begin{array}{r}
2 \mathrm{Cl}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
\end{array} \underbrace{4 \mathrm{HCl}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})}_{\text {Products }}
$$

$$
\begin{aligned}
& \Delta H^{\circ}=\left\{\left[4 \Delta H_{\mathrm{f}}^{\circ}(\mathrm{HCl}(\mathrm{~g}))\right]+\left[\Delta H_{\mathrm{f}}^{\circ}\left(\mathrm{O}_{2}(\mathrm{~g})\right)\right]\right\} \\
& -\left\{\left[2 \Delta H_{\mathrm{f}}^{\circ}\left(\mathrm{Cl}_{2}(\mathrm{~g})\right)\right]+\left[2 \Delta H_{\mathrm{f}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right)\right]\right\}
\end{aligned}
$$

$$
\Delta H^{\circ}=\{[4(-92.31)]+[(0.00)]\}-\{[2(0.00)]+[2(-285.8)]\}
$$

$$
\Delta H^{\circ}=\{4(-92.31)\}-\{[2(-285.8)]\}
$$

$$
\Delta H^{\circ}=\{4(-92.31)\}-\{[2(-285.8)]\}=
$$

$$
-369.24+571.6=202.4 \mathrm{~kJ}
$$

## An Introduction to Free Energy

## Gibbs Free-Energy Change ( $\Delta$ G)

Enthalpy of
Reaction kJ/mol (- $\Delta \mathrm{H}$ spontaneous) reaction releases heat
$\Delta \mathrm{G}=$ negative
$\Delta \mathrm{H}=$ negative
$\Delta \mathrm{S}=$ positive

## End 1/15 Wed

C section

## An Introduction to Free Energy

## Gibbs Free-Energy Change ( $\Delta$ G)

$$
\begin{array}{|l|l|l}
\Delta G=\Delta H-\mathrm{T} \Delta S & \begin{array}{l}
\text { high T: } \\
\text { low } \mathrm{T}: ~
\end{array} \Delta \mathrm{~S} \text { decides } \\
\text { lecides }
\end{array}
$$

$\Delta G<0 \quad$ Process is spontaneous. (rxn goes $\rightarrow$ )
$\Delta G=0 \quad$ Process is at equilibrium
(neither spontaneous nor nonspontaneous).
$\Delta G>0 \quad$ Process is nonspontaneous. (rxn goes $\leftarrow)$

## Chapter 11

HW 11.2: Phase Changes between Solids, Liquids, \& Gases
$\Delta H_{\text {fusion }}$ solid to a liquid $\quad \Delta H_{\text {vap }}$ liquid to a gas
At phase change (melting, boiling, etc) :
$\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S} \quad \& \quad \mathrm{G}=$ zero (bc 2 phases in equilibrium)
$\Delta \mathrm{H}=\mathrm{T} \Delta \mathrm{S}$
a. BP of ethanol is $78.4^{\circ} \mathrm{C} \Delta \mathrm{H}_{\text {vap }}=38.56 \mathrm{~kJ} / \mathrm{mol}$. What is the entropy change for the vaporization ( $\Delta \mathrm{S}_{\text {vap }}$ in $\mathrm{J} /(\mathrm{Kmol})$ ?
$\Delta \mathrm{S}=\Delta \mathrm{H} / \mathrm{T}=38.56 \mathrm{~kJ} / \mathrm{mol} /\left(78.4^{\circ} \mathrm{C}+273.15\right) \mathrm{K}=$
$\Delta \mathrm{S}=38.56 \mathrm{~kJ} / 351.55(\mathrm{~mol} \mathrm{~K})=0.10969 \mathrm{~kJ} /(\mathrm{mol} \mathrm{K})=110 \mathrm{~J} /(\mathrm{mol} \mathrm{K})$
b. $\mathrm{CHCl}_{3}$ has $\Delta \mathrm{H}_{\text {vap }}=29.2 \mathrm{~kJ} / \mathrm{mol}$ and $\Delta \mathrm{S}_{\text {vap }}=87.5 \mathrm{~J} /(\mathrm{K} \mathrm{mol})$. What is the BP of the $\mathrm{CHCl}_{3}$ in Kelvin ?

## End C sect 1/21 Tuesday

# Phase Changes between Solids, Liquids, and Gases Heating Curve for Water 


(d) *Vaporizing liquid water: $\Delta \mathrm{H}_{\text {vap }}=+40.67 \mathrm{~kJ} / \mathrm{mol}$ largest energy for process
(e) Heating water vapor from $100^{\circ} \mathrm{C}$ to $125^{\circ} \mathrm{C}$ :

Molar heat capacity of water vapor $=33.6 \mathrm{~J} / \mathrm{mol}{ }^{\circ} \mathrm{C}$ $33.6 \mathrm{~J} / \mathrm{mol}{ }^{\circ} \mathrm{C} * 25^{\circ} \mathrm{C}=0.840 \mathrm{~kJ} / \mathrm{mol}$

$$
\begin{aligned}
& \mathrm{q}=\mathrm{n} * \mathrm{C}_{\mathrm{m}} * \Delta \mathrm{~T} \\
& \mathrm{q}=\mathrm{n} \Delta \mathrm{H}_{\text {fus }} \\
& \mathrm{q}=\mathrm{n} \Delta \mathrm{H}_{\text {vap }}
\end{aligned}
$$

## For the same molecule:

Largest $\Delta \mathbf{S}$ for gaseous form of compound
Medium $\quad \Delta \mathrm{S}$ for liquid form of compound
Smallest $\Delta \mathrm{S}$ for solid form of compound

## For a Reaction:

Largest $\Delta \mathbf{S}$ for the side of the reaction with larger number of gaseous molecules.

$$
\begin{aligned}
\text { ex: } 2 \mathrm{H}_{2}(\mathrm{~g})+ & \mathrm{O}_{2}(\mathrm{~g})
\end{aligned} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \mathrm{r}
$$

## Kinds of Solids

Amorphous Solids: Particles are randomly arranged and have no ordered long-range structure. examples: rubber, window glass, plastic, butter

Crystalline Solids: Particles have an ordered arrangement extending over a long range.

- ionic solids (ex: $\mathrm{NaCl}, \mathrm{BaF}_{2}$ )
- molecular (covalent molecule) solids (ex: $\mathrm{C}_{12} \mathrm{H}_{26}, \mathrm{I}_{2}$, naphthalene, sucrose)
- covalent network solids (ex: carbon, silicon dioxide)
- metallic solids (ex: metallic Fe, metallic Na, metallic Pt, etc)

HW 11.5: Phase Diagrams Fill in the blank with a letter
(a) Solid
(d) line transition $s \rightarrow$ I
(b) Liquid
(e) line transition I $\rightarrow$ g
(c) Gas
(f) line transition $s \rightarrow g$


## Chapter 12

## HW 12.1: Energy Changes and the Solution Process

Like dissolves Like
Match the following for solutes which will BEST dissolve in solvents. Fill in the blank with letters. Blank may have more than one letter. (asking for most soluble may be soluble in more than one solvent)
solute
(a) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$
(b) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}$
(c) NaCl
(d) $\mathrm{CH}_{2} \mathrm{Cl}_{2}$
solvents
(1) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}$
(2) $\mathrm{H}_{2} \mathrm{O}$
(3) $\mathrm{CH}_{3} \mathrm{Cl}$


## Concentration Units for Solutions

$$
\text { Molarity }(\mathbf{M})=\frac{\text { Moles of solute }}{\text { Liters of solution }}
$$

Mole fraction $(\boldsymbol{X})=\frac{\text { Moles of component }}{\text { Total moles making up solution }}$

$$
\text { Mass percent }=\frac{\text { Mass of component }}{\text { Total mass of solution }} \times 100 \%
$$

$$
\text { Molality }(m)=\frac{\text { Moles of solute }}{\text { Mass of solvent }(\mathrm{kg})}
$$

Physical Behavior of Solutions: Colligative Properties Colligative Properties: Properties that depend on the amount of a dissolved solute but not on its chemical identity (usually non volatile solute)

- Vapor-pressure lowering ( $\left.\mathrm{P}_{\text {solution }}=i^{*} \mathrm{P}_{\text {solvent }}{ }^{*} \mathrm{X}_{\text {solvent }}\right)$ (Raoult's Law)
- Boiling-point elevation ( $\left.\Delta \mathrm{T}_{\mathrm{b}}=i^{*} \mathrm{~K}_{\mathrm{b}}{ }^{*} \mathrm{~m}\right)$
- Freezing-point depression $\left(\Delta \mathrm{T}_{\mathrm{f}}=-i^{*} \mathrm{~K}_{\mathrm{f}}{ }^{*} \mathrm{~m}\right)$
- Osmotic pressure ( $\Pi=i^{*} \mathrm{M}^{*} \mathrm{R}^{*} \mathrm{~T}$ )
$X=$ mole fraction
$i=$ van't Hoff factor (=1 for nonelectrolytes) (= \# of ions in solution per formula) $\mathrm{m}=$ molality
$\mathrm{K}_{\mathrm{b}}$ molal BP constant, $\mathrm{K}_{\mathrm{f}}$ molal FP constant
$\mathrm{M}=$ molarity
$R=$ gas constant $=0.08206 \mathrm{~L}$ atm $/(\mathrm{mol} \mathrm{K})$


## Chapter 13

## Reaction Rates

General Reaction:

$$
a \mathrm{~A}+b \mathrm{~B} \longrightarrow d \mathrm{D}+e \mathrm{E}
$$

$$
\text { rate }=\begin{array}{ll}
\begin{array}{l}
-\frac{1}{a} \frac{\Delta[\mathrm{~A}]}{\Delta t}=-\frac{1}{b} \frac{\Delta[\mathrm{~B}]}{\Delta t} \\
\begin{array}{l}
\text { disappearing reactant } \\
\text { (negative sign) }
\end{array}
\end{array} & \begin{array}{l}
\frac{1}{d} \frac{\Delta[\mathrm{D}]}{\Delta t}=\frac{1}{e} \frac{\Delta[\mathrm{E}]}{\Delta t} \\
\text { appearing product } \\
\text { (positive sign) }
\end{array} \\
\hline
\end{array}
$$

reaction: $\quad 2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \longrightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g)$

$$
\text { rate }=\begin{array}{|l}
-\frac{1}{2} \frac{\Delta\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]}{\Delta t}=\frac{1}{4} \frac{\Delta\left[\mathrm{NO}_{2}\right]}{\Delta t}=\frac{\Delta\left[\mathrm{O}_{2}\right]}{\Delta t} \\
\begin{array}{l}
\text { disappearing } \\
\text { reactant }
\end{array} \\
\text { appearing product }
\end{array}
$$

## Rate Laws and Reaction Order

Rate Law: An equation that shows the dependence of the reaction rate on the concentration of each reactant
$a \mathrm{~A}+b \mathrm{~B} \longrightarrow$ products
rate $\alpha[\mathrm{A}]^{m}[\mathrm{~B}]^{n}$
rate $=k[A]^{m}[B]^{n}$
$k$ is the rate constant.

$$
\mathrm{m}, \mathrm{n} \neq \mathrm{a}, \mathrm{~b}
$$

## HW 13.3: Experimental Determination of a Rate Law

Given the following experimentally determined rate law: what is the overall order of the reaction?
(a) Rate $=\mathrm{k}[\mathrm{A}][\mathrm{B}]^{2} \quad \underline{3}$
(b) Rate $=\mathrm{k}\left[\mathrm{BrO}_{3}^{-}\right]\left[\mathrm{Br}{ }^{-}\right]\left[\mathrm{H}^{+}\right]^{2}$


End 2/14
Friday C section
(c) Rate $=\mathrm{k}[\mathrm{A}]^{2}$

2

Note additional questions not in HW:
Order of [B] in (a) is? 2
Order of [A] in (a) is? 1
Order of [A] in (c) is ? 2

## (integrated rate law - summary of last few slides)

TABLE 13.4 Characteristics of Zeroth-, First-, and Second-Order Reactions of the Type A $\rightarrow$ Products

|  | Zeroth-Order | First-Order | Second-Order |
| :--- | :--- | :--- | :--- |
| Rate law | $-\frac{\Delta[\mathrm{A}]}{\Delta t}=k$ | $-\frac{\Delta[\mathrm{A}]}{\Delta t}=k[\mathrm{~A}]$ | $-\frac{\Delta[\mathrm{A}]}{\Delta t}=k[\mathrm{~A}]^{2}$ |
| Integrated Rate Law | $[\mathrm{A}]_{t}=-k t+[\mathrm{A}]_{0}$ | $\ln [\mathrm{~A}]_{t}=-k t+\ln [\mathrm{A}]_{0}$ | $\frac{1}{[\mathrm{~A}]_{t}}=k t+\frac{1}{[\mathrm{~A}]_{0}}$ |
| Linear graph | $[\mathrm{A}]$ versus $t$ | $\ln [\mathrm{~A}]$ versus $t$ | $\frac{1}{[\mathrm{~A}]}$ versus $t$ |
| $\mathbf{y}=\mathbf{m X}+\mathbf{b}$ | $[\mathrm{A}]_{0}$ | Slope $=-k$ | $\ln [\mathrm{~A}]_{0}$ |
| eqn Of line | $[\mathrm{A}]$ |  | $\frac{1}{[\mathrm{~A}]}$ |

Graphical

$$
k=-(\text { Slope })
$$

$k=-($ Slope $)$
$k=$ Slope
determination of $k$

| Half-life | $t_{1 / 2}=\frac{[\mathrm{A}]_{0}}{2 k}$ | $t_{1 / 2}=\frac{0.693}{k}$ | $t_{1 / 2}=\frac{1}{k[\mathrm{~A}]_{0}}$ |
| :--- | :--- | :--- | :--- |
|  | (not constant) | (constant) | (not constant) |

$t_{1 / 2}=\frac{1}{k[\mathrm{~A}]_{0}}$
(not constant)

## HW 13.7: Rate Laws for Elementary Reactions (reaction mechanism steps)

For the following elementary reactions (reaction mechanism steps) give the rate law and the molecularity of the reaction mechanism step (unimolecular, bimolecular, trimolecular, etc.)
(a) $\mathrm{CH}_{3} \mathrm{Br}+\mathrm{OH}^{-} \rightarrow \mathrm{Br}-+\mathrm{CH}_{3} \mathrm{OH}$
(b) $\mathrm{O}_{3} \rightarrow \mathrm{O}_{2}+\mathrm{O}$
(c) $\mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{HO}_{2}$
(d) $\mathrm{NO}_{2}+\mathrm{F} \rightarrow \quad \mathrm{NO}_{2} \mathrm{~F}$
(e) $2 \mathrm{ClO} \rightarrow \mathrm{Cl}_{2} \mathrm{O}_{2}$

End 2/24 Monday A section
$\underline{\text { rate }}=k\left[\mathrm{CH}_{3} \underline{\mathrm{Br}]}\right]\left[\mathrm{OH}^{-}\right]$
bimolecular
rate $=k\left[\mathrm{O}_{3}\right]$
unimolecular
rate $=\mathrm{k}\left[\mathrm{H}_{2} \underline{\mathrm{O}}_{2}\right]\left[\mathrm{OH}^{-}\right]$, bimolecular
$\underline{\text { rate }}=\mathrm{k}\left[\mathrm{NO}_{2}\right][\mathrm{F}]$
bimolecular
$\underline{\text { rate }}=\mathrm{k}[\mathrm{ClO}]^{2}$
bimolecular

## Chapter 14

HW 14.1: The Equilibrium Constant $K_{c}$
Write the equilibrium constant expression for the
following reactions. ( $\mathrm{K}_{\mathrm{p}}=$ equilibrium constants with amounts are given by pressure of each component)(if gas is in solution use $\mathrm{K}_{\mathrm{c}}$, if gas is in gas state use $\mathrm{K}_{\mathrm{p}}$ )

$$
a \mathrm{~A}+b \mathrm{~B} \rightleftharpoons c \mathrm{C}+d \mathrm{D} \quad K_{\mathrm{c}}=\frac{[\mathrm{C}]^{[ }[\mathrm{D}]^{d}}{[\mathrm{~A}]^{d}[\mathrm{~B}]^{b}} \quad \begin{aligned}
& \text { (s) or (1) } \\
& \text { leave out of } \\
& \text { K expression }
\end{aligned}
$$

(a) 2 BrCl (soln) $\underset{\leftarrow}{\underset{ }{*} \mathrm{Br}_{2} \text { (soln) }+\mathrm{Cl}_{2} \text { (soln) } \quad K_{\mathrm{c}}=\frac{\left[\mathrm{Br}_{2}\right]\left[\mathrm{Cl}_{2}\right]}{\left[\mathrm{BrCl}^{2}\right.}{ }^{2}}$
(b) $2 \mathrm{~N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \underset{\leftarrow}{\rightarrow} 4 \mathrm{NO}(\mathrm{g})$ (give $\mathrm{K}_{\mathrm{p}}$ )

$$
K_{p}=\frac{\left(\mathrm{P}_{\mathrm{NO}}\right)^{4}}{\left(\mathrm{P}_{\mathrm{N} 2}\right)^{2}\left(P_{\mathrm{O} 2}\right)^{2}}
$$

(c) $\mathrm{BaSO}_{4}(\mathrm{~s}) \underset{\leftarrow}{\underset{\leftarrow}{~}} \mathrm{Ba}^{2+}(\mathrm{aq})+\mathrm{SO}_{4}{ }^{2-(\mathrm{aq})} \quad K_{\mathrm{c}}=\left[\mathrm{Ba}^{2+}\right]\left[\mathrm{SO}_{4}{ }^{2-}\right]$
(d) $\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+3 \underset{\leftarrow}{\underset{\leftarrow}{\mathrm{CO}(\mathrm{g})}} 2 \mathrm{Fe}(\mathrm{s})+3 \mathrm{CO}_{2}(\mathrm{~g}) \underset{\text { 2/28 Friday }}{ } \quad K_{p}=\frac{\left(\mathrm{P}_{\mathrm{CO2}}\right)^{3}}{\left(\mathrm{P}_{\mathrm{co}}\right)^{3}}$

The Equilibrium Constant $K_{\mathrm{c}}$
The equilibrium constant and the equilibrium constant expression are for the chemical equation as written.

$$
a \mathrm{~A}+b \mathrm{~B} \rightleftharpoons c \mathrm{C}+d \mathrm{D} \quad K_{\mathrm{c}}=\frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{~A}]^{a}[\mathrm{~B}]^{b}}
$$

## End 2/28F A section

(a) $\mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g) \rightleftharpoons 2 \mathrm{NH}_{3}(g)$ reverse rxn
(b) $2 \mathrm{NH}_{3}(g) \rightleftharpoons \mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g)$ reversed rxn (a) - turn K upside down
(c) $2 \mathrm{~N}_{2}(g)+6 \mathrm{H}_{2}(g) \rightleftharpoons 4 \mathrm{NH}_{3}(g)$ doubled rxn (a) - square all terms

$$
K_{\mathrm{c}}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}
$$

double rxn

$$
\begin{aligned}
& K_{\mathrm{c}}^{\prime}=\frac{\left[\mathrm{N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}{\left[\mathrm{NH}_{3}\right]^{2}}=\frac{1}{K_{\mathrm{c}}} \\
& K_{\mathrm{c}}^{\prime}=\frac{\left[\mathrm{NH}_{3}\right]^{4}}{\left[\mathrm{~N}_{2}\right]^{2}\left[\mathrm{H}_{2}\right]^{6}}=K_{\mathrm{c}}^{2}
\end{aligned}
$$

## HW 14.4: The Equilibrium Constant $K_{\mathrm{c}}$

 $K_{\mathrm{p}}=K_{\mathrm{c}}(R T)^{\Delta n} \quad \boldsymbol{R}$ is the gas constant, $0.08206 \frac{\mathrm{Latm}}{\mathrm{Kmol}}$.$\Delta \mathrm{n}=(\mathrm{c}+\mathrm{d})-(\mathrm{a}+\mathrm{b})$

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})+\mathrm{CH}_{4}(\mathrm{~g}) \underset{\leftarrow}{\leftarrow} \mathrm{CO}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})
$$

End 3/2 Monday A section

If $\mathrm{K}_{\mathrm{c}}=3.8 \times 10^{-3}$ at 1000 K , what is the value of $\mathrm{K}_{\mathrm{p}}$ ?
$\mathrm{K}_{\mathrm{p}}=\mathrm{K}_{\mathrm{c}}(\mathrm{RT})^{\Delta \mathrm{n}}$
$\Delta \mathrm{n}=(1+3)-(1+1)=2$
$\mathrm{K}_{\mathrm{p}}=\left(3.8 \times 10^{-3}\right)[(0.08206 \mathrm{Latm} / \mathrm{mol} \mathrm{K})(1000 \mathrm{~K})]^{2}$
$\mathrm{K}_{\mathrm{p}}=25.588=26$

## HW 14.5: Using the Equilibrium Constant

- If $Q_{\mathrm{c}}<K_{\mathrm{c}}$ net reaction goes from left to right (reactants to products, $\rightarrow$ ).
- If $Q_{\mathrm{c}}>K_{\mathrm{c}}$ net reaction goes from right to left (products to reactants, $\leftarrow$ ).
- If $Q_{\mathrm{c}}=K_{\mathrm{c}}$ no net reaction occurs. (at equilibrium)

If the equilibrium constant $\mathrm{K}_{\mathrm{c}}=2.78 \times 10^{-10}$ and you have a reaction $\mathrm{A}+2 \mathrm{~B} \rightarrow 3 \mathrm{C}+\mathrm{D}$ and $[\mathrm{A}]=1.78 \times 10^{-4}, \quad[\mathrm{~B}]=1.1 \times 10^{-5}$ and $[\mathrm{C}]=1.23 \times 10^{-6},[\mathrm{D}]=7.8 \times 10^{-8}$ does the reaction go forward to produce more products or backwards to produce more reactant or stay in equilibrium?

$$
\mathrm{Kc}=\frac{[\mathrm{C}]^{3}[\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]^{2}} \quad \mathrm{Q}=\frac{\left[1.23 \times 10^{-6}\right]^{3}\left[7.8 \times 10^{-8}\right]}{\left[1.78 \times 10^{-4}\right]\left[1.1 \times 10^{-5}\right]^{2}}
$$

$$
\mathrm{Q}=6.74 \times 10^{-12} \& 6.74 \times 10^{-12}<2.78 \times 10^{-10}
$$

Reaction goes forward until equilibrium is reached.
End 3/2/20

## HW 14.6: Using the Equilibrium Constant

For $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{l}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g})$, for initial concentrations of $\mathrm{H}_{2}(0.00623 \mathrm{M}), \mathrm{l}_{2}$ ( 0.00414 M ) and $\mathrm{HI}(0.0224 \mathrm{M})$. Calculate the concentrations at equilibrium given $K_{\text {c }}$ (54.3) assuming forward rxn.
(a) Set up the ICE table. (where $x=$ change of $\mathrm{H}_{2}$ )
(b) show the expression for Kc
(c) If your solution to Kc gives $x=0.00156$, calculate the concentration of HI .
$\mathrm{H}_{2}(g)+\mathrm{I}_{2}(g) \rightleftharpoons 2 \mathrm{HI}(g)$

| 0.00623 | 0.00414 | 0.0224 |
| :---: | :---: | :---: |
| Initial |  |  |
| $-x$ | $-x$ | $+2 x$ |
| Change |  |  |
| $0.00623-x$ | $0.00414-x$ | $0.0224+2 x$ |
| Equilibrium |  |  |
|  |  |  |
| $\mathrm{Kc}=\frac{[0.0224+2 \mathrm{x}]^{2}}{[0.00623-\mathrm{x}][0.00414-\mathrm{x}]}=54.3$ |  |  |

Solution $\mathrm{x}=0.00156 \quad[\mathrm{Hl}]=\mathbf{0 . 0 2 2 4}+\mathbf{2}(\mathbf{0 . 0 0 1 5 6})=\mathbf{0 . 0 2 5 5} \mathbf{M}$

HW 14.7: Le Châtelier's Principle: If a stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress. (equilibrium shifts to undo stress applied to system)
$2 \mathrm{~A}(\mathrm{~g})+\mathrm{B}(\mathrm{g}) \rightarrow 3 \mathrm{C}(\mathrm{g})+2 \mathrm{D}(\mathrm{g}) \Delta \mathrm{H}=$ negative (circle one parenthesis under which direction will equilibrium shift each letter) hint: $\Delta \mathrm{H}$ negative is exothermic $=(+$ heat, heat is product $)$
(a) add $\mathrm{A} \quad$ rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(b) remove B rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(c) add C rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(d) remove C rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(e) higher $T \quad$ rxn goes $[(\rightarrow)$ or $(\leftarrow)]$ end Test $3(\mathrm{e}) \&$ below
(higher $\mathrm{T}=$ add heat)
(f) higher P rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(assume all reactants \& products in reaction are gases) (moves to fewer moles gas)
(g) higher V rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(assume all reactant \& products in reaction are gases) (moves to fewer moles gas)

## Chapter 15

# HW 15.1: Acid-Base Concepts: Arrhenius \& BrønstedLowry Theory (conjugate acid/base) 

Given the following equation of acid/base dissociation. Give the Acid/Conjugate Base, Base/Conjugate Acid pairs.
$\mathrm{HNO}_{3}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{NO}_{3}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
Acid $\mathrm{H} \mathrm{NO}_{3}$ Conjugate Base $\mathrm{NO}_{3}{ }^{-}$
Base $\mathrm{H}_{2} \mathrm{O}$ Conjugate Acid $\mathrm{H}_{3} \mathrm{O}^{+}$
$\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{NH}_{4}{ }^{+}+\mathrm{OH}^{-}$
Base $\mathrm{NH}_{3}$ Conjugate Acid $\mathrm{NH}_{4}{ }^{+}$
Acid $\mathrm{H}_{2} \mathrm{O}$ Conjugate Base $\mathrm{OH}^{-}$
$\mathrm{HNO}_{3}+\mathrm{NaOH} \rightarrow \mathrm{NaNO}_{3}+\mathrm{H}_{2} \mathrm{O}$
Acid $\mathrm{H} \mathrm{NO}_{3}$ Conjugate Base $\mathrm{NO}_{3}$
Base NaOH Conjugate Acid $\mathrm{H}_{2} \mathrm{O}$
Do this HW by emailing the answer in the text of your email instead of taking a photo of your answer on paper.

## The pH Scale



## The pH Scale Equations

$$
\begin{aligned}
& \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right] \\
& \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \\
& \mathrm{pK}_{\mathrm{w}}=-\log \mathrm{K}_{\mathrm{w}} \\
& \mathrm{~K}_{\mathrm{w}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1 \times 10^{-14} \\
& \mathrm{pK}_{\mathrm{w}}=\mathrm{pH}+\mathrm{pOH}=14
\end{aligned}
$$

## HW 15.2: The pH Scale

(a) What is the pH of a solution of $\left[\mathrm{H}^{+}\right]=2.3 \times 10^{-2}$
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \left(2.3 \times 10^{-2}\right)=-(-1.638)=1.64$
(b) What is the pOH of a solution of $[\mathrm{OH}-]=7.7 \times 10^{-3}$ $\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=-\log \left(7.7 \times 10^{-3}\right)=-(-2.11)-2.11$
(c) What is the pH of the solution in (b) above ?
$\mathrm{pH}+\mathrm{pOH}=14 \quad \mathrm{pH}+2.11=14 \quad \mathrm{pH}=11.9$
(d) What is the $\left[\mathrm{H}^{+}\right]$of the solution in (c) above ?
$\left[\mathrm{H}^{+}\right]=\operatorname{antilog}(-\mathrm{pH})=\operatorname{antilog}(-11.9)=1.26 \times 10^{-12}$

Answer this HW by writing the text of the answer into your email instead of uploading photo.

## HW 15.3: The pH in Solutions of Strong Acids and Strong Bases

Just use concentration of strong acid or base bc dissociates completely.
a. What is the pH of a 0.053 M solution of HCl ? $\mathrm{pH}=-\log (0.053)=(1.28)$
a. What is the pH of a solution of 0.150 M solution of NaOH ? $\mathrm{pOH}=-\log (0.150 \mathrm{M})=-(-0.823)$ $\mathrm{pH}=14-0.823=13.2$

Answer this HW by writing the text of the answer into your email instead of uploading photo.

## Equilibria in Solutions of Weak Acids

$\mathrm{HA}(a q)+\mathrm{H}_{2} \mathrm{O}(\Lambda) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{A}^{-}(a q)$
Acid-Dissociation Constant: $K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$

For Weak Acids and Weak Bases MUST USE K ${ }_{\mathrm{a}} / \mathrm{K}_{\mathrm{b}}$

## HW 15.4: Calculating Equilibrium Concentrations of Weak Acids

Calculate the pH of a 0.10 M HCN solution. At $25^{\circ} \mathrm{C}, K_{\mathrm{a}}$ $=4.9 \times 10^{-10}$.
$\mathrm{HCN}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{\prime}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{CN}^{-}(\mathrm{aq})$

| 0.10 |  | $\approx 0$ | 0 |
| :---: | :--- | :---: | :---: |
|  |  | $+x$ | $+x$ |
| $0.10-x$ |  | $x$ | $x$ |

$$
K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CN}^{-}\right]}{[\mathrm{HCN}]}
$$

## Chapter 16

## HW 16.1: Neutralization Reactions

(a) Give the neutralization reaction for the following acid / base reaction
$\mathrm{HF}+\mathrm{KOH} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{KF} \quad$ molecular rxn
$\mathrm{HF}+\mathrm{K}^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{K}^{+}+\mathrm{F}^{-}$total ionic
$\mathrm{HF}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{F}^{-}$net ionic rxn
(b) Is the product of the neutralization. [ (acidic) (basic) (neutral)] (choose one)
$\mathrm{K}+$ is neutral, F - is weak base so weak base

## The Common-Ion Effect

Calculate the pH of a solution that is prepared by dissolved 0.10 mol of acetic acid and 0.10 mol sodium acetate in enough water to make 1.00 L of solution. $\mathrm{Ka}=1.8 \times 10^{-5}$
$\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\Lambda) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}(\mathrm{aq})$

| 0.10 |  | $\approx 0$ | 0.10 |
| :---: | :---: | :---: | :---: |
|  |  | $+x$ | $+x$ |
| $0.10-x$ |  | $x$ | $0.10+x$ |

$$
K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]}
$$

## Buffer Solutions

Buffer Solution: A solution that contains a weak acid and its conjugate base and resists drastic changes in pH

Weak acid

$$
+
$$



## HW 16.3: Buffer Solutions

What is the pH of a buffer solution with 0.25 M HF and 0.50 M NaF . $\mathrm{Ka}=3.5 \times 10^{-4}$. What is the pH after the addition of 0.002 $\mathrm{mol} \mathrm{HNO}_{3}$ ?

$$
\mathrm{HF}^{(a q)}+\mathrm{H}_{2} \mathrm{O}(\Lambda) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{F}^{-}(a q)
$$

Using Henderson - Hasselbalch:

$$
\mathrm{pH}=\mathrm{pKa}+\log \frac{[\text { base }]}{[\text { acid }]}=-\log \left(3.5 \times 10^{-4}\right)+\log \frac{0.50}{0.25}
$$

$$
\mathrm{pH}=3.456+0.30=3.757
$$

## HW 16.4: Buffer Solutions

Buffer Solution: A solution that contains a weak acid and its conjugate base and resists drastic changes in pH

Given the following reagents, fill the blank with the other molecule needed to make a buffer solution and label each as (A) for acid or (B) for base.

1. $\left.\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{A}) \quad \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}-\mathrm{B}\right)$
2. $\mathrm{CN}^{-}$( B ) $\mathrm{HCN}(\mathrm{A})$
3. $\mathrm{NH}_{3}(\mathrm{~B}) \quad \mathrm{NH}_{4}^{+}(\mathrm{A})$

# Weak Acid-Strong Base Titrations <br> $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}(\mathrm{aq})$ 



## HW 16.4: pH Titration Curves

Label the following titration curve as (A) strong acid added to strong base (B) strong base added to strong acid (C) strong base added to weak acid (choose one letter under each \#)

1.(A)(B)(C)

2.(A)(B)(C)

3.(A)(B)(C)

## Measuring $K_{\text {sp }}$ and Calculating Solubility from $K_{\text {sp }}$

Calculate the molar solubility of $\mathrm{MgF}_{2}$ in water at $25^{\circ} \mathrm{C}$.

$$
\operatorname{MgF}_{2}(s) \rightleftharpoons \mathrm{Mg}^{2+}(a q)+2 \mathrm{~F}^{-}(a q)
$$



$$
\begin{gathered}
K_{\mathrm{sp}}=7.4 \times 10^{-11}=\left[\mathrm{Mg}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}=(x)(2 x)^{2} \\
4 x^{3}=7.4 \times 10^{-11}
\end{gathered}
$$

$$
x=\left[\mathrm{Mg}^{2+}\right]=\text { Molar solubility }=2.6 \times 10^{-4} \mathrm{M}
$$

## HW 16.6: Measuring $K_{\text {sp }}$ and Calculating Solubility from $K_{\text {sp }}$

Calculate the molar solubility of Ag Cl in water at $25^{\circ} \mathrm{C}$.

$$
\mathrm{Ag} \mathrm{Cl}(s) \rightleftharpoons \mathrm{Ag}^{+}(a q)+\mathrm{Cl}^{-}(a q)
$$



$$
\begin{gathered}
K_{\mathrm{sp}}=1.8 \times 10^{-10}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]=(x)(x) \\
x^{2}=1.8 \times 10^{-10}
\end{gathered}
$$

$$
x=\left[\mathrm{Ag}^{+}\right]=\text {Molar solubility }=1.3 \times 10^{-5} \mathrm{M}
$$

## Chapter 18

## Balancing Redox Reactions by the Half-Reaction Method (in acidic solution)

Step 1. Write the unbalanced net ionic equation.

Step 2. Decide which atoms are oxidized and which are reduced, and write the two unbalanced half-reactions.

Step 3. Balance both half-reactions for all atoms except O and H .

Step 4. Balance each half-reaction for O by adding water to the side with less O , and balance for H by adding $\mathrm{H}^{+}$to the side with less H .


Step 5. Balance each half-reaction for charge by adding electrons to the side with greater positive charge, and then multiply by suitable factors to make the electron count the same in both half-reactions.

Step 6. Add the two balanced half-reactions together, and cancel electrons and other species that appear on both sides of the equation.

Check your answer by making sure the equation is balanced both for atoms and for charge.

## 18.1: Balancing Redox Reactions: The Halfi-Reaction Method


(a) Oxidation half-reaction: $\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(a q)+2 \mathrm{e}^{-}$
(b) Reduction half-reaction: $\mathrm{Cu}^{2+}(a q)+2 \mathrm{e}^{-} \longrightarrow \mathrm{Cu}(s)$

Balanced redox reaction:

$$
\mathrm{Zn}(s)+\mathrm{Cu}^{2+}(a q) \longrightarrow \mathrm{Zn}^{2+}(a q)+\mathrm{Cu}(s)
$$

HW 18.2: Balancing Redox Reactions: The Half-Reaction Method (acidic solution) +3 e

(a) Oxidation half-reaction: $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(a q)+2 \mathrm{e}^{-}$
(b) Reduction half-reaction: $\mathrm{NO}_{3}^{-}(a q)+3 \mathrm{e}^{-} \longrightarrow \mathrm{NO}(g)$
(c) Balanced redox reaction:

$$
2 \mathrm{NO}_{3}^{-}(\mathrm{aq})+8 \mathrm{H}^{+}+3 \mathrm{Cu}(s) \quad \rightarrow \quad 2 \mathrm{NO}(g)+3 \mathrm{Cu}^{+2}(a q)+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

