## ENERGY

- thermodynamics: the study of energy transfer

Conservation of energy: Energy may change form, but the overall amount of energy remains constant. "first law of thermodynamics"

- ... but what IS energy?
- energy is the ability to do "work"

个 motion of matter

Kinds of energy?

- Kinetic energy: energy of matter in motion $E_{K}=\frac{1}{2} \overbrace{V^{2}}^{m u s s}$
- Potential energy: energy of matter that is being acted on by a field of force (like gravity)

- What sort of energy concerns chemists? Energy that is absorbed or released during chemical reactions.
- Energy can be stored in chemicals ... molecules and atoms. INTERNAL ENERGY: "U"
$\uparrow$ related to the kinetic and potential energy of atoms, molecules, and their component parts.
- We measure energy transfer ... which is called HEAT. (HEAT is the flow of energy from an area of higher temperature to an area of lower temperature)

Q: heat
SYSTEM: the object or material under study
SURROUNDINGS: everything else

| Type of process | Energy is ... | Sign of $Q$ | Temp of SURROUNDINGS ... |
| :--- | :--- | :---: | :---: |
| ENDOTHERMIC | transferred from <br> SURROUNDINGS <br> to SYSTEM | + | decreases |
| EXOTHERMIC | transferred from <br> SYSTEM to <br> SURROUNDINGS | - | increases |



$$
\mathrm{HCl}(\mathrm{aq})+\mathrm{NaOH}(a q) \rightarrow \mathrm{Na}\left(l(a q)+\mathrm{H}_{2} \mathrm{O}(\ell)\right.
$$

This reaction is EXOTHERMIC. Energy is transferred from the reactants and products (the SYSTEM) to the water in the flask, the flask itself, etc. (the SURROUNDINGS)

$$
3 \mathrm{M} \mathrm{NaOH}, 25^{\circ} \mathrm{C}
$$



This reaction is ENDOTHERMIC. Energy is transferred from the room/flask/etc. (the SURROUNDINGS) to the reaction itself (the SYSTEM).

$$
\begin{aligned}
& \mathrm{NH}_{3}, \mathrm{H}_{2} \mathrm{O}_{1} \\
& \mathrm{Bu}^{\left.\left(\mathrm{NO}_{2}\right)\right)_{2}\left(\mathrm{aq}_{2}\right), \mathrm{CO}} \mathrm{C}
\end{aligned}
$$

## ENERGY UNITS

- calorie (cal): the amount of energy required to change the temperature of one gram of water by one degree Celsius (or Kelvin)

$$
\sim_{0^{\circ}}^{1 g}|\rightarrow| \sim \sim_{\substack{\text { add one } \\ \text { calorie of } \\ \text { energy }}}^{1 g} \mid \text { lg } \mid m \text { For waiter }
$$

- Calories in food? The "Calorie" that is given on American food labels is actually the kilocalorie (kcal)
- Joule (J): SI unit for energy. It's defined based on the equation for kinetic energy.

$$
I=1=\frac{\mathrm{Kg} \mathrm{~m}^{2}}{s^{2}} \text {, from }
$$


$4.184 \mathrm{~J}=1 \mathrm{cal}$

- the Joule is a small unit. For most reactions at lab scale, we'll use kilojoules (kJ).

CALORIMETRY - measurement of heat

$$
\mathrm{HCl}(\text { aq })+\mathrm{NaOH}(\text { aq }) \rightarrow \mathrm{H}_{2} \mathrm{O}(\ell)+\mathrm{NaCl}_{(\text {aq })}
$$

50. mL
2.0 M HCl

## The acid and base

 solutions are mostly water ... we'll assume that the two solutions are essentially pure water for heat transfer purposes...
50. mL
2.0 M NaOH

Assuming that no heat is lost from the water to the surrounding air,

... if we knew something about the WATER, we could use that to find the heat of the REACTION!

SPECIFIC HEAT

- a measured quantity. The amount of energy required to change the temperature of one gram of a particular substance by one degree Celsius.
- Specific heat information for common substances is readily available. For water,

$$
Q=1.000 \frac{\mathrm{cal}}{\mathrm{~g}^{\circ} \mathrm{C}}
$$

- For objects, like reaction vessels, you might know the HEAT CAPACITY, which is the amount of energy required to change the temperature of an object by one degree Celsius

$$
\begin{gathered}
\text { Units: } \mathrm{J} / \mathrm{o}^{\circ} \mathrm{C} \text { or cal /o } \mathrm{C} \\
Q=C \times \triangle \\
c=\text { heat capacity }
\end{gathered}
$$

$$
\left.\mathrm{HCl}(\mathrm{aq})+\mathrm{NaOH}(\text { aq }) \rightarrow \mathrm{H}_{2} \mathrm{O}(l)+\mathrm{NaCl}_{\text {(aq }}\right)
$$

50. mL
2.0 M HCl

The acid and bsae solutions are mostly water ... we'll assume that the two solutions are essentially pure water for heat transfer purposes...


Initial temperature of solutions: $\qquad$ $\frac{21.7^{\circ}}{35.0^{\circ}} \mathrm{C}$

$$
\begin{aligned}
Q_{r}+Q_{w}=0 \quad Q_{w}=m_{\omega} \times S_{w} \times \Delta T_{w}=(100 . g)\left(4.184 \frac{5}{g^{\circ} \mathrm{C}}\right)\left(35.0^{\circ} \mathrm{C}-21.7^{\circ} \mathrm{C}\right) \\
Q_{w}=5 S 64.72 \mathrm{~J} \\
Q_{r}+5564.772 \mathrm{~J}=0 ; Q_{r}=-5564.72 \mathrm{~J}
\end{aligned}
$$

To report the energy change in this reaction to others, we should express it in terms of heat transfer per mole of something. A different amount of reactant would

$$
\begin{aligned}
& \text { have a different Q } \\
& \quad \text { mull } \mathrm{HCl}: 0.050 L \times \frac{2.0 \mathrm{mulHCl}}{L}=0.10 \mathrm{mul} \mathrm{HCl} \\
& Q_{r \times n}=\frac{Q_{r}}{\text { mulesHCl}}=\frac{-5564.22 \mathrm{~J}}{0.10 \mathrm{mul} H C l}=-56000 \frac{\mathrm{~J}}{\mathrm{~mol}}=-56 \frac{\mathrm{HJ}}{\mathrm{~mol}}
\end{aligned}
$$

One problem ..
PATH. The amount of energy required for a process depends on how the process is carried out.

Example: Driving from Florence to Columbia. How much energy is required? (gas) Jeep Cherokee ( 15 mpg ) vs Toyota Prius ( 43 mpg ). The Jeep will use much more fuel than the Prius even though they start and end at the same place. So the fuel usage is what we call a PATH FUNCTION, while the location is a STATE FUNCTION.

- so the heat of reaction depends on how the reaction is done.
- we need (for reporting) some kind of standard condition. At constant pressure, we can define a state function called ENTHALPY (H)

$$
\begin{gathered}
H=U+P V \\
\Delta H=Q_{\text {cuastuat pressure }}
\end{gathered}
$$

... we record the "enthalpy change of reaction" in our data books.


SINCE the enthalpy change does NOT depend on path, this means that we can use standard values for enthalpy to predict the heat change in reactions that we have not tested in a calorimeter.

THERMOCHEMICAL EQUATIONS

- are like regular chemical equations, except that phase labels are REQUIRED and the enthalpy for the reaction is given.

$$
\mathrm{CH}_{3} \mathrm{COCH}_{3}(l)+4 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 3 \mathrm{CO}_{2}(g)+3 \mathrm{H}_{2} \mathrm{Ol}(\mathrm{l}) ; \mathrm{A}=-1800 \mathrm{~kJ}
$$

- Why are phase labels required? Because phase changes either absorb or release energy.
$\Delta H=-1800$ KJ ... what does this mean?

$$
\begin{aligned}
1 \mathrm{~mol} \mathrm{CH}_{3} \mathrm{COCH}_{3} & =-1800 \mathrm{~kJ} \\
4 \mathrm{mul} \mathrm{O}_{2} & =-1800 \mathrm{~kJ} \\
3 \mathrm{mul} \mathrm{CO}_{2} & =-1800 \mathrm{~kJ} \\
3 \mathrm{mul} \mathrm{H}_{2} \mathrm{O} & =-1800 \mathrm{~kJ}
\end{aligned}
$$

We treat the enthalpy change as if it's another product of the reaction!

A few more terms related to enthalpy:

- Enthalpy of vaporization / heat of vaporization: The enthalpy change on vaporizing one mole of a substance. (from liquid to vapor)
- Enthalpy of fusion / heat of fusion: The enthalpy change when a mole of liquid changes to the solid state.
$\mathrm{CH}_{3} \mathrm{COCH}_{3}(l)+4 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 3 \mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2} \mathrm{Ol}(\mathrm{l}) ; \Delta H=-1800 \mathrm{~kJ}$ What would be the enthapy change when 25 g of water are produced by the reaction?

1 - Convert 25 g water to moles using FORMULA WEIGHT.
2 - Convert moles water to ENTHALPY CHANGE using THERMOCHEMICAL EQUATION

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{O}: 18.016 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}=\mathrm{md} \mathrm{H}_{2} \mathrm{O} \\
& 2 \mathrm{mgol} \mathrm{H}_{2} \mathrm{O}=-1800 \mathrm{~kJ} \\
& 2 \mathrm{H} \times \frac{\mathrm{mdH}}{18.016 \mathrm{gH}_{2} \mathrm{O}} \times \frac{-1800 \mathrm{~kJ}}{3 \mathrm{~mol} \mathrm{H}}=-830 \mathrm{~kJ}
\end{aligned}
$$

This is an EXOTHERMIC reaction. Energy is transferred out of the system (the reaction) and to the surroundings. Not that surprising if you realize that this is a COMBUSTION reaction!
-830 kJ is also equal to the HEAT $(Q)$, provided we burn the acetone at constant pressure!

- A reaction that forms exactly one mole of the specified substance from its elements at their STANDARD STATE at 25 C and 1 atm pressure.
you may see fractional coefficients in these formation reactions, because you MUST form exactly one mole of the product!
- The heat of formation for an element in its standard state at 25C and 1 atm is ZERO.

$$
\Delta H_{f, O_{2}}^{0}(g)=O \mathrm{~kJ} / \mathrm{mol}
$$

- What are formation reactions good for?
... finding enthalpies for more interesting reactions!

$$
\begin{aligned}
& \begin{array}{c}
\mathrm{CO}_{2}(\mathrm{~g}): C(\mathrm{~s}, \text { graphite })+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow\left(\mathrm{O}_{2}(\mathrm{~g}) ; \Delta 4=-393,5 \mathrm{kj}\right. \\
L_{\text {heat of formation of carbon dioxide }} \Delta H_{f}^{0} \text { or } \Delta H_{f}
\end{array} \\
& C O(g): C(s, g r a p h i t e)+\frac{1}{2} O_{2}(g) \rightarrow(O(g) ; \Delta H=-110.5 \mathrm{~kJ}
\end{aligned}
$$

Let's say we would like to find the enthalpy of reaction for this equation:
$2 \mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \xrightarrow{\longrightarrow} \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) ; \Delta H=? \quad$ From
Hess' Law: If you add two reactions to get a new reaction, their enthalpies also add. そ ert


Hess' Law using enthalpy of formation:

$$
\begin{aligned}
& \Delta H=\sum_{0} \Delta H_{f, \text { projects }}-\sum_{-393,5} \Delta H_{f_{1} \text { reacherts }}^{-241.8} \\
& 2 \mathrm{C}_{2}^{226.7} \mathrm{H}_{2}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 4 \mathrm{CO}_{2}^{-393,5}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) ; \Delta \mathrm{H}=\text { ? } \\
& \Delta H=[4(-393.5)+2(-241.8)]-[2(226.7)+5(0)] \\
& =-25 \| k J
\end{aligned}
$$

See Appendix C in the textbook for enthalpy of formation data: p A-8 to A-1 1

* Remember:
- Multiply each enthalpy by its stoichiometric coefficient from the reaction
- Enthalpy of formation of an element at its standard state is zero
- Watch phase labels. You will usually find SEVERAL enthalpies of formation for a given substance in different phases!
- For ionic substances in solution, remember that they exist as free ions, so look up the aqueous IONS!

Example problems:
FORMULA WEIGHTS in $\mathrm{g} / \mathrm{mol}$

$$
2 \mathrm{H}_{2}^{2.016} 32.00(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) ; \Delta \mathrm{H}=-484 \mathrm{~kJ}
$$

Calculate the enthalpy change for the combustion of 1.00 kg of hydrogen gas.
1 - Convert 1.00 kg of hydrogen gas to moles using FORMULA WEIGHT
2 - Convert moles hydrogen gas to enthalpy change using THERMOCHEMICAL EQUATION

$$
\begin{aligned}
& 2.016 \mathrm{~g} \mathrm{H}=\text { mol } \mathrm{H}_{2}\left|2 \mathrm{~mol} \mathrm{H}_{2}=-484 \mathrm{~kJ}\right| \mathrm{Kg}=10^{3} \mathrm{~g} \\
& 1.00 \mathrm{~kg} \mathrm{H}_{2} \times \frac{10^{3} \mathrm{~g}}{\mathrm{~kg}} \times \frac{\mathrm{mol} \mathrm{H}}{2.016 \mathrm{~g} \mathrm{H}} \times \frac{-484 \mathrm{~kJ}}{2 \mathrm{~mol} \mathrm{H}}=\begin{array}{l}
-120000 \mathrm{~kJ} \\
\text { per } \mathrm{kg} \mathrm{H}
\end{array}
\end{aligned}
$$

$$
4 \mathrm{NH}_{3}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 4 \mathrm{NO}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) ; \Delta H=-906 \mathrm{~kJ}
$$

What is the enthalpy change when 150 . L of nitrogen monoxide are formed by this reaction at 25.0 C and 1.50 atm pressure?
1 - Convert 150. L of NO to moles using IDEAL GAS EQUATION
2 - Convert mol NO to enthalpy change using THERMOCHEMICAL EQUATION

$$
\begin{aligned}
& \text { (1) PV=nRT } \quad P=1.50 \text { atm } \quad V=150 . L \\
& n=\frac{P V}{R T} \left\lvert\, R=0.08206 \frac{\mathrm{Lam}}{\mathrm{~mol} \cdot \mathrm{Kc}} T=25.0^{\circ} \mathrm{C}=298.2 \mathrm{~K}\right. \\
& n_{\text {NO }}=\frac{(1.50 \mathrm{arm})(150 . \mathrm{L})}{\left(0.08206 \frac{\mathrm{Lam}}{\mathrm{~mol} \cdot \mathrm{k}}\right)(298.2 \mathrm{~K})}=9.194822849 \mathrm{mul} \mathrm{NO} \\
& 4 \mathrm{~mol} N O=-906 \mathrm{~kJ} \\
& 9.194822849 \mathrm{mul} \mathrm{NO} \times \frac{-906 \mathrm{~kJ}}{4 \mathrm{mul} \mathrm{NO}}=-2080 \mathrm{~kJ}
\end{aligned}
$$

${ }_{16} \quad 34.086 \mathrm{~g} / \mathrm{mol} \quad$ Heat of formation / enthalpy of formation!

$$
\left.\begin{array}{c}
\begin{array}{c}
0 \\
-20.50 \\
2 \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow
\end{array} 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{SO}_{2}(\mathrm{~g})
\end{array}\right] \Delta H_{f}^{0}, \mathrm{rJ} / \mathrm{mol}
$$

What is the enthalpy change at standard conditions when 25.0 grams of hydrogen sulfide gas is reacted?
1 - Calculate the enthalpy change for the reaction AS WRITTEN with HESS'S LAW
2 - Convert 25.0 grams hydrogen sulfide to moles using FORMULA WEIGHT.
3 - Convert moles hydrogen sulfide to enthalpy change using THERMOCHEMICAL EQUATION.

$$
\begin{aligned}
\Delta H & =\sum \Delta H_{f, p r o d u c t s}^{0}-\sum \Delta H_{\text {e, reactants }}^{0} \\
& =[2(-288.8)+2(-246.8)]-[2(-20.80)+3(0)] \\
& =-1124.2 \mathrm{~kJ}
\end{aligned}
$$

So the THERMOCHEMICAL EQUATION is ...

$$
\begin{aligned}
& \frac{2 \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{SO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}=-1124.2 \mathrm{~kJ}}{34.086 \mathrm{~g} \mathrm{H}_{2} \mathrm{~S}=\mathrm{mol}_{2} \mathrm{~S} \mid 2 \mathrm{~mol} \mathrm{H}} \mathrm{H}_{2} \mathrm{~S}=-1124.2 \mathrm{~kJ} \\
& 2 \mathrm{~S} .0 \mathrm{~g} \mathrm{H}
\end{aligned}
$$

$$
\mathrm{C}_{3} \mathrm{H}_{8}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 3 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) ; \Delta \mathrm{H}=-2043 \mathrm{~kJ}
$$

Calculate the volume of propane gas at 25.0 C and 1.08 atm required to provide 565 kJ of heat using the reaction above. Propane: $\mathrm{C}_{3} \mathrm{H}_{8}$

1 - Convert the energy requirement to moles propane using THERMOCHEMICAL EQUATION 2 - Convert moles propane to volume using IDEAL GAS EQUATION

$$
\begin{aligned}
& \mathrm{mol}_{3} \mathrm{C}_{3} \mathrm{H}_{8}=-2043 \mathrm{~kJ} \quad \begin{array}{l}
\text { Since the reaction is the SYSTEM here, the energy } \\
\text { requirement has }
\end{array} \\
& \text { requirement has a NEGATIVE sign (it's LOSING, or } \\
& -565 \mathrm{~kJ} \times \frac{\operatorname{mol} C_{3} \mathrm{H}_{8}}{-2043 \mathrm{LJ}}=0.2765540871 \mathrm{~mol}_{3} \mathrm{C}_{8} \\
& P V=n R T \quad P=1.08 \text { atm } R=0.08206 \frac{\mathrm{l} \text { atm }}{\mathrm{mol} \cdot \mathrm{k}} \\
& V=\frac{n R T}{P} \left\lvert\, \begin{array}{l}
T=25.0^{\circ} \mathrm{C}=298.2 \mathrm{~K} \\
n=0.2765540871 \mathrm{~mol}_{3} \mathrm{H}_{8}
\end{array}\right. \\
& V=\frac{\left(0.2765540871 \mathrm{~mol} \mathrm{C}_{3} \mathrm{Hg}\right)\left(0.08206 \frac{\mathrm{~L}-\mathrm{atm}}{\mathrm{mul} \cdot \mathrm{k}}\right)(298.2 \mathrm{k})}{(1.08 \mathrm{~atm})} \\
& =6.27 \mathrm{~L} \mathrm{C}_{3} \mathrm{H}_{8} \Leftrightarrow 28.08 \mathrm{Catm}
\end{aligned}
$$

