

Ch 5

Thermochemistry

- definition - a part of thermodynamics (study of energy & its transformations) that involves the relationships b/w chemical reactions and energy changes involving heat

- Energy - capacity to do work or transfer heat

↓
energy used
to make an object
w/mass move against
a force

↓
energy used
to cause the
temp. of an object
to increase

1. How can matter have energy?

- A. through motion Kinetic Energy

$$KE = \frac{1}{2}mv^2$$

m = mass (kg)
v = velocity (m/s)

- B. through its position relative to other objects

Potential Energy

$$PE = mgh$$

m = mass (kg)
g = gravity (9.8 m/s²)
h = height (m)

really only
useful for larger
objects, not atoms
& molecules!

- C. through energy of attraction

Electrostatic Potential Energy

$$E_{el} = \frac{kQ_1Q_2}{d}$$

k = 8.99 × 10⁹ Jm/C²
Q₁ & Q₂ = charged particles
d = distance b/w particles

• If Q₁ & Q₂ have the same sign (+ or -), E_{el} will be +
∴ the charges repel each other.

• If Q₁ & Q₂ have opposite signs, E_{el} will be -
∴ the charges attract each other.

- The lower E_{el} is, the more stable the system is!
∴ The stronger the opposite charges are, the stronger,
more stable the system is!

What does that really mean?

(1) Find E_{el} of a system with $1p^+$ & $1e^-$

$$E_{el} = \frac{kQ_1Q_2}{d}$$

$$E_{el} = \frac{(8.99 \times 10^9 \text{ Jm/C}^2)(1.602 \times 10^{-19} \text{ C})(-1.602 \times 10^{-19} \text{ C})}{2.36 \times 10^{-10} \text{ m}}$$

$$E_{el} = -9.78 \times 10^{-19} \text{ J}$$

$$Q_{p^+} = +1.602 \times 10^{-19} \text{ C}$$

$$Q_{e^-} = -1.602 \times 10^{-19} \text{ C}$$

$$d = .236 \text{ nm}$$

$$(1 \text{ m} = 1 \times 10^9 \text{ nm})$$

$$.236 \text{ nm} \left(\frac{1 \text{ m}}{1 \times 10^9 \text{ nm}} \right) = 2.36 \times 10^{-10} \text{ m}$$

Find E_{el} of a system with $2p^+$ & $2e^-$.

$$E_{el} = \frac{(8.99 \times 10^9 \text{ Jm/C}^2)(2 \times 1.602 \times 10^{-19} \text{ C})(2 \times 1.602 \times 10^{-19} \text{ C})}{9.6 \times 10^{-11} \text{ m}}$$

$$E_{el} = -9.61 \times 10^{-18} \text{ J}$$

$$d = 96 \text{ pm} \quad (1 \text{ m} = 1 \times 10^{12} \text{ pm})$$

$$96 \text{ pm} \left(\frac{1 \text{ m}}{1 \times 10^{12} \text{ pm}} \right) = 9.6 \times 10^{-11} \text{ m}$$

2. Units for Energy

• SI unit \rightarrow Joule (J)

$$1 \text{ J} = \frac{1 \text{ kg m}^2}{\text{s}^2}$$

• calorie (cal)

$$1 \text{ cal} = 4.184 \text{ J}$$

• nutritional Calorie (Cal)

$$1 \text{ Cal} = 1000 \text{ cal} = 1 \text{ kcal}$$

(2) What is the kinetic energy, in J and cal, of an Argon atom moving with a speed of 650 m/s? (Hint: $1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$)
How about a mole of Ar atoms?

$$KE = \frac{1}{2}mv^2$$

$$KE = \frac{1}{2}(6.632 \times 10^{-26} \text{ kg})(650 \text{ m/s})^2$$

$$KE = 1.40 \times 10^{-20} \text{ kg m}^2/\text{s}^2 =$$

$$KE = 1.40 \times 10^{-20} \text{ J/atom}$$

$$m_{Ar} = 39.95 \text{ amu} \left(\frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)$$

$$M_{Ar} = 6.632 \times 10^{-26} \text{ kg}$$

$$1.40 \times 10^{-20} \text{ J} \left(\frac{1 \text{ cal}}{4.184 \text{ J}} \right) = 3.35 \times 10^{-21} \text{ cal}$$

$$1.40 \times 10^{-20} \frac{\text{J}}{\text{atom}} \left(\frac{6.02 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \right) = 8428 \text{ J/mol}$$

(2)

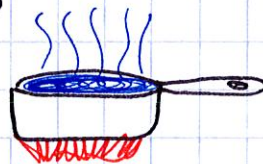
Some terms to know:

- system - part of the universe singled out for study
- surroundings - everything else in the universe

Types of systems

A. open system - matter & energy can be exchanged w/ the surroundings

Ex. pot of H₂O boiling on a stove



B. closed system - energy (only) can be exchanged w/ the surroundings

Ex. an instant heat pack or cold pack



↑ type we study most often!

C. isolated system - neither energy nor matter can be exchanged w/ the surroundings

Ex. an insulated thermos



3. How is energy transferred?

Work & Heat

A. work

$$w = F \cdot d$$

w = work
F = force

d = distance

B. heat - transfer of energy from a hotter object to a colder object.

4. The First Law of Thermodynamics - Energy is conserved in every process!

Any energy lost by a system must be gained by the surroundings and vice versa!

A. Internal Energy (E) - the sum of all the KE & PE of all the components of a system

- hard to directly measure, easier to find change in internal energy (ΔE)

$$\Delta E = E_f - E_i$$

- ΔE has 3 parts

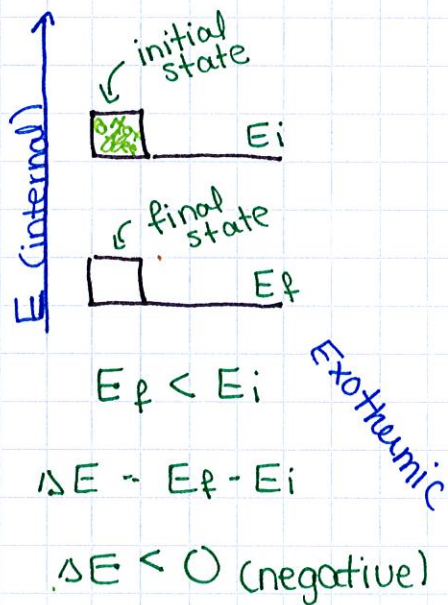
1) a number

2) a unit

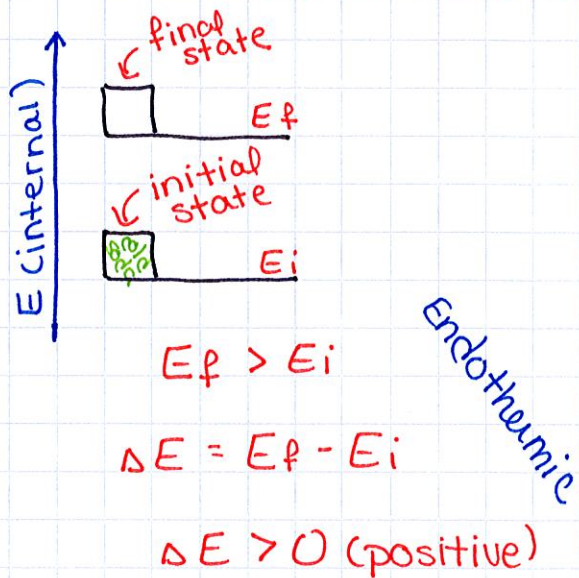
3) a sign (+ or -)

give the magnitude of the change

gives the direction of the change (into/out of the system)

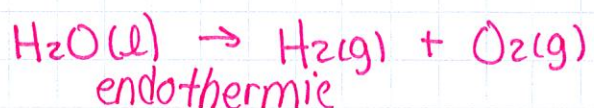
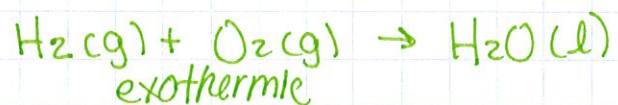
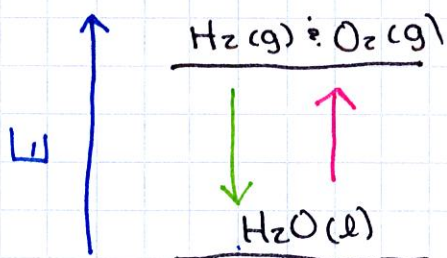


energy is lost to the surroundings

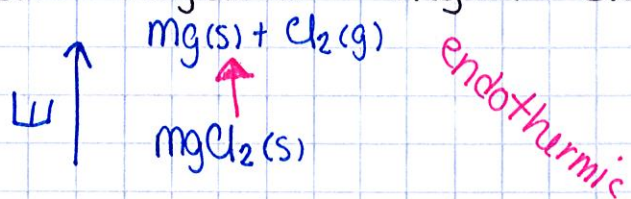


energy is gained from the surroundings

Energy Diagram



(3) The internal energy for $\text{Mg}(s)$ and $\text{Cl}_2(g)$ is greater than that of $\text{MgCl}_2(s)$. Sketch an energy diagram that represents the reaction: $\text{MgCl}_2(s) \rightarrow \text{Mg}(s) + \text{Cl}_2(g)$.



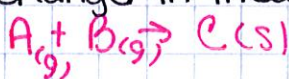
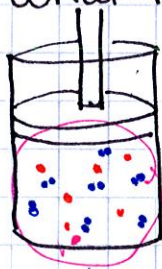
B. Relating ΔE to Heat & Work

$$\Delta E = q + w$$

Sign Conventions

q	+ system gained heat	- system lost heat
w	+ work done on the system	- work done by the system
ΔE	+ net gain of energy by the system	- net loss of energy by the system

(4) Gases A & B are confined in a cylinder/piston arrangement. A & B react to form solid C in the reaction: $A(g) + B(g) \rightarrow C(s)$. As the reaction occurs, the system loses 1150 J of heat to the surroundings and the surroundings do 480 J of work on the system as the piston moves downward when the solid forms. What is the change in internal energy?



$$\Delta E = q + w$$

$$q = -1150 \text{ J}$$

$$w = +480 \text{ J}$$

$$\Delta E = -1150 \text{ J} + +480 \text{ J} = -670 \text{ J}$$

(5) Calculate the change in internal energy for a process in which the system absorbs 140 J of heat from the surroundings and does 85 J of work on the surroundings.

$$\Delta E = q + w$$

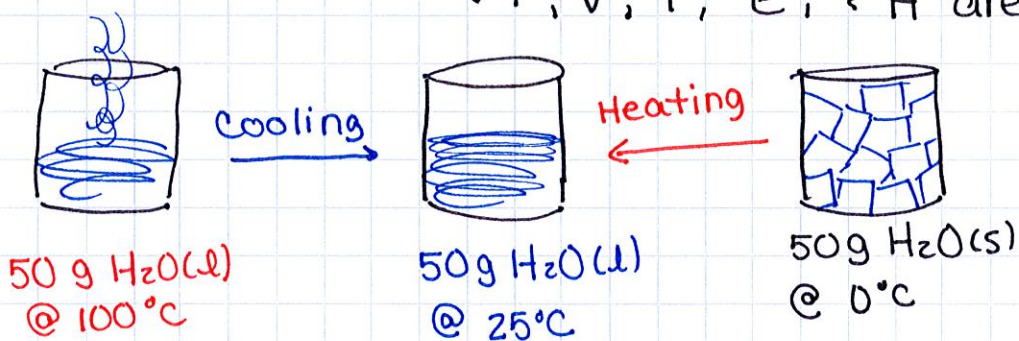
$$q = +140 \text{ J}$$

$$w = -85 \text{ J}$$

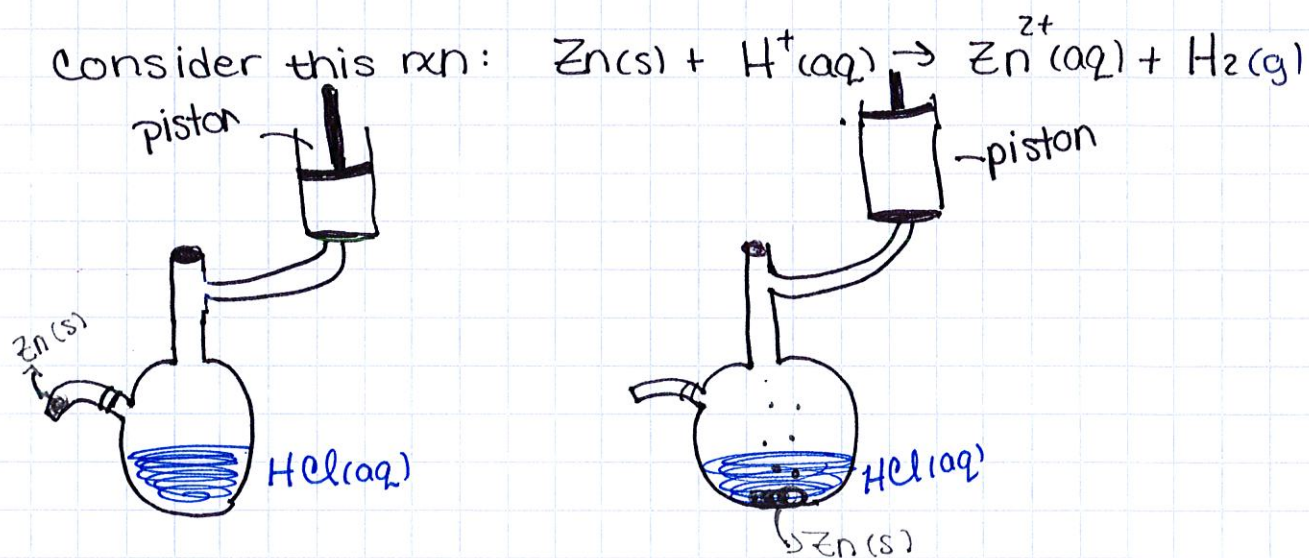
$$\Delta E = +140 \text{ J} + -85 \text{ J} = +55 \text{ J}$$

more terms.

- endothermic - process when heat flows into the system from the surroundings (Ex. melting ice)
- exothermic - process when heat flows from (exits) the system to the surroundings.
- state function - a property of a system that is determined by the state or condition of the system & not by how it got to that state. Its value is fixed when temp., pressure, composition, and physical form are specified
 - $P, V, T, E, \& H$ are state functions



5. Enthalpy (H) - heat flow in processes occurring @ constant pressure when no forms of work other than P - V work are done.



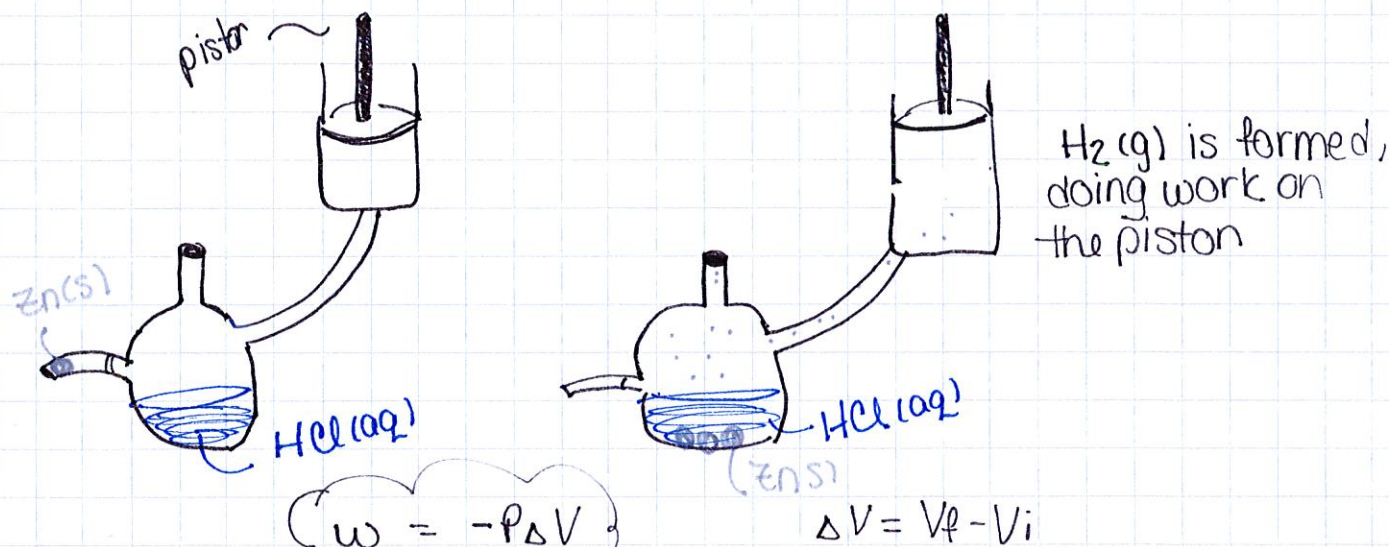
$H_2(g)$ being formed does work on the piston, raising it.

$$w = -P \Delta V$$

$$\Delta V = V_f - V_i$$

5. Enthalpy (H) - heat flow in processes occurring @ constant pressure when no work other than P - V work are done

Consider this reaction: $Zn(s) + H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$



$$H = E + PV$$

$$\Delta H = \Delta(E + PV)$$

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta E = q + w$$

$$w = -P\Delta V$$

$$\Delta H = (q + w) - w$$

$$\Delta H = q_p$$

Enthalpy - heat @ constant P

$$\Delta H > 0$$

endothermic

$$\Delta H < 0$$

exothermic

Enthalpy

$$H = E + PV$$

∴

$$\Delta H = \Delta(E + PV)$$
$$\Delta H = \Delta E + P\Delta V$$

$$\Delta E = q + w$$
$$w = -P\Delta V$$

$$\Delta H = (q_p + w) - w$$

$$\Delta H = q_p$$

enthalpy = heat @ constant P

ΔH is positive \rightarrow endothermic

ΔH is negative \rightarrow exothermic

(6) Determine the sign of ΔH under constant P in each process:

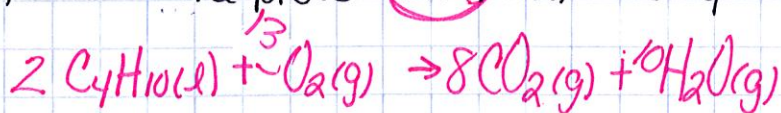
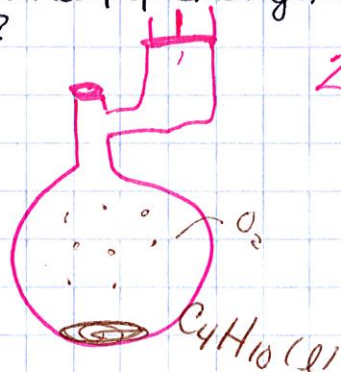
1) An ice cube melts

$+\Delta H$

2) 1g butane is combusted in sufficient oxygen to give complete combustion to CO_2 & H_2O .

$-\Delta H$

3) Suppose that 1g of butane & enough oxygen are placed in a cylinder piston arrangement. The cylinder is insulated so no heat can escape. A spark initiates combustion, which forms carbon dioxide and water vapor. If we used this apparatus to measure enthalpy change, would the piston rise, fall, or stay the same?



b. Enthalpies of Reaction

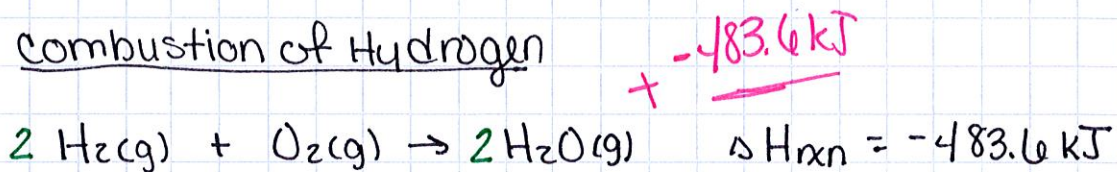
$$\Delta H = H_f - H_i$$

for a chemical reaction...

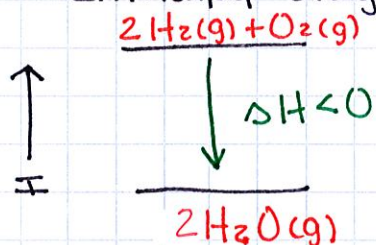
$$\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$$

$$\Delta H_{\text{rxn}} = H_p - H_r$$

Combustion of Hydrogen

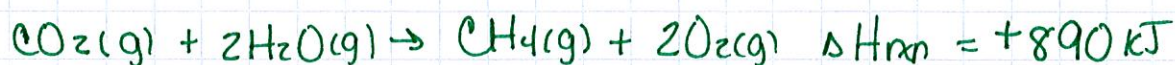
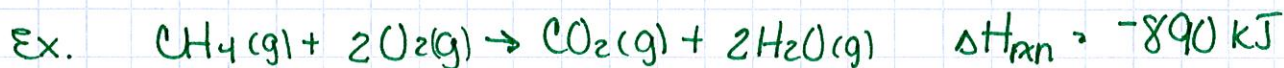


Enthalpy Diagram



Guidelines

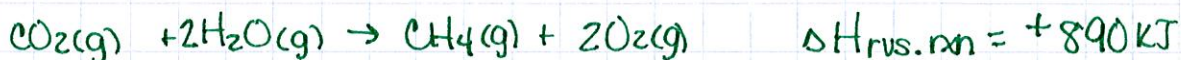
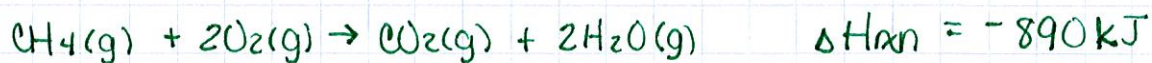
- 1) Enthalpy is an extensive property.
↳ dependent on the amount of reactant consumed!
- 2) ΔH_{rxn} is equal in magnitude, but opposite in sign, to $\Delta H_{\text{rev. rxn}}$.



- 3) ΔH_{rxn} depends on the state of the reactants and products.

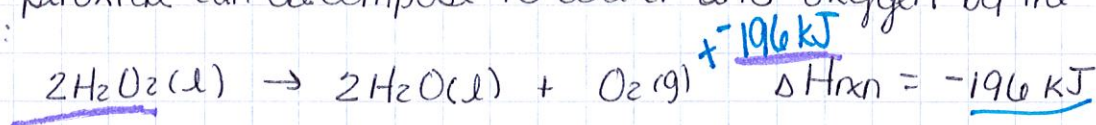
Guidelines

- 1) Enthalpy is an extensive property
↳ depends on how much of the reactant is consumed in a reaction.
- 2) ΔH_{rxn} is equal in magnitude, but opposite in sign to the reverse reaction.



3. ΔH_{rxn} depends on the states of matter of the reactants and products

Ex (8) Hydrogen peroxide can decompose to water and oxygen by the reaction:



Calculate the value of q when 5.00g of H_2O_2 decomposes at constant pressure.

$$5.00 \text{ g H}_2\text{O}_2 \left(\frac{1 \text{ mol H}_2\text{O}_2}{34 \text{ g H}_2\text{O}_2} \right) = .147 \text{ mol H}_2\text{O}_2 \left(\frac{-196 \text{ kJ}}{2 \text{ mol H}_2\text{O}_2} \right) = -14.4 \text{ kJ}$$

Ex (9) Consider the reaction: $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{MgO}(\text{s})$ $\overset{+1204 \text{ kJ}}{\Delta H_{\text{rxn}} = -1204 \text{ kJ}}$

Calculate the amount of heat transferred when 2.4g. Mg reacts at constant pressure.

$$2.4 \text{ g Mg} \left(\frac{1 \text{ mol Mg}}{24 \text{ g Mg}} \right) \left(\frac{-1204 \text{ kJ}}{2 \text{ mol Mg}} \right) = -60.2 \text{ kJ}$$

How many grams of $\text{MgO}(\text{s})$ are produced during an enthalpy change of -96.0 kJ ?

$$-96.0 \text{ kJ} \left(\frac{2 \text{ mol MgO}}{-1204 \text{ kJ}} \right) \left(\frac{40 \text{ g MgO}}{1 \text{ mol MgO}} \right) = 6.38 \text{ g MgO}$$

7. Calorimetry - measurement of heat flow

• heat capacity C - amount of heat needed to raise an object's temperature by 1 K (or 1°C).

- C_m (molar heat capacity) - heat capacity of 1 mol of a substance

- C_s (specific heat capacity) - heat capacity of 1 g of a substance

$$C_s = \frac{\text{(quantity of heat transferred)}}{\text{(grams of substance)(change in temp.)}}$$

$$C_s = \frac{q}{m \cdot \Delta T}$$

$$q = m C_s \Delta T$$

Ex (10) Large beds of rocks are used in some solar-heated homes to store heat. Assume the specific heat capacity of the rocks is $.82 \text{ J/gK}$.

(A) Calculate the quantity of heat absorbed by 50.0 kg of rock if the temperature increased by 12.0°C .

$$\begin{aligned} q &= ? \\ m &= 50.0 \text{ kg} = 5 \times 10^4 \text{ g} \\ C &= .82 \text{ J/gK} \\ \Delta T &= 12.0^\circ\text{C} = 12.0 \text{ K} \end{aligned}$$

$$q = (5 \times 10^4 \text{ g})(.82 \text{ J/gK})(12.0 \text{ K})$$

$$q = 492,000 \text{ J}$$

(B) What temperature change would these rocks undergo if they emit 450 kJ of heat?

$$\begin{aligned} q &= -450 \text{ kJ} = -450,000 \text{ J} \\ m &= 5 \times 10^4 \text{ g} \\ C &= .82 \text{ J/gK} \\ \Delta T &= ? \end{aligned}$$

$$-450,000 \text{ J} = (5 \times 10^4 \text{ g})(.82 \text{ J/gK}) \Delta T$$

$$\frac{-450,000 \text{ J}}{(5 \times 10^4 \text{ g})(.82 \text{ J/gK})} = \Delta T$$

$$\Delta T = -10.98 \text{ K}$$

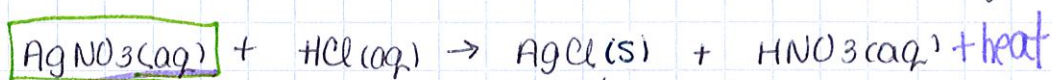
$$\Delta T = -10.98 \text{ K}$$

A. Constant-Pressure Calorimetry "Coffee-Cup" Calorimetry
 - no physical boundary b/w the system (reaction) and the surroundings (calorimeter + water + universe)

∴ All heat gained by the solution is produced by the reaction

$$-q_{\text{rxn}} = q_{\text{soln.}} = m_{\text{soln.}} C_{\text{soln.}} \Delta T$$

Ex (11) When 50.0 mL of .100 M AgNO_3 and 50.0 mL of .100 M HCl are mixed in a coffee-cup calorimeter, the temperature increases from 22.30°C to 23.11°C . The temperature increase is caused by the reaction:



Calculate ΔH for this reaction, in kJ/mol AgNO_3 , assuming the combined solution has a mass of 100.0 g and a specific heat of $4.18 \text{ J/g}^\circ\text{C}$.

soln.

$$q = ?$$

$$m = 100.0 \text{ g}$$

$$C = 4.18 \text{ J/g}^\circ\text{C}$$

$$\Delta T = 23.11^\circ\text{C}$$

$$-22.30^\circ\text{C}$$

$$.81^\circ\text{C}$$

$$q_{\text{soln.}} = (100.0 \text{ g})(4.18 \text{ J/g}^\circ\text{C})(.81^\circ\text{C}) = 338.58 \text{ J} = .339 \text{ kJ}$$

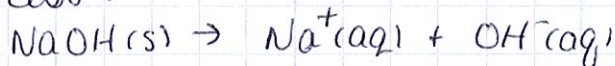
$$n_{\text{AgNO}_3} = .100 \text{ M} \cdot .0500 \text{ L} = .005 \text{ mol AgNO}_3$$

$$.339 \text{ kJ}$$

$$.005 \text{ mol AgNO}_3$$

$$= -67.8 \text{ kJ/mol AgNO}_3$$

Ex (12) When a 9.55 g sample of solid sodium hydroxide dissolves in 100.0 g of water in a coffee cup calorimeter, the temperature rises from 23.6°C to 47.4°C . Calculate ΔH (in kJ/mol NaOH) for the process:



Assume the specific heat for the solution is $4.18 \text{ J/g}^\circ\text{C}$.

$$q_{\text{soln.}} = ?$$

$$m = 100.0 \text{ g} + 9.55 \text{ g} = 109.5 \text{ g}$$

$$C = 4.18 \text{ J/g}^\circ\text{C}$$

$$\Delta T = 47.4^\circ\text{C}$$

$$-23.6^\circ\text{C}$$

$$23.8^\circ\text{C}$$

$$q_{\text{soln.}} = (109.5 \text{ g})(4.18 \text{ J/g}^\circ\text{C})(23.8^\circ\text{C})$$

$$= 10898 \text{ J} = 10.90 \text{ kJ}$$

$$\Delta H = \frac{-10.90 \text{ kJ}}{.239 \text{ mol NaOH}} = -45.6 \text{ kJ/mol NaOH}$$