

## Quiz

A 42.8 mL solution of ammonia ( $\text{NH}_3$ ) is titrated with a solution of 0.9713 M hydrochloric acid. The initial reading on the buret containing the HCl was 47.13 mL and the final reading when the endpoint was reached was 12.94 mL.

Determine the concentration of the  $\text{NH}_3$  solution.

## Chemical Thermodynamics

- *Thermodynamics* is the study of the energetics and order of a system.
- A *system* is the thing we want to study—it can be a chemical reaction, a solution, an automobile, or the universe.
- Everything else is included in the *surroundings*—the system may interact with the surroundings or be isolated from the surroundings.

## Chemical Thermodynamics

- The system is described by a set of variables that represent the state of the system—these are called *state variable*.
- Common state variables are temperature, pressure, and volume.
- The distinguishing feature of state variables is that when a change of state occurs, the path taken in the change does not effect the final result.

## Chemical Thermodynamics

Example: raise the temperature of a piece of metal from 298 K to 1000 K.

- Path 1—first put metal in liquid nitrogen and cool to 77 K, then heat in a flame to 1000 K.
- Path 2—directly heat with flame from 298 K to 1000 K.

The final result of 1000 K does not depend on which path you take—the metal is still at 1000 K.

## Changes of State

- A physical change of state does not alter the chemical identity of the system. Examples of physical changes of state include: freezing, melting, vaporization, expansion of a gas.
- A chemical change of state alters the chemical identity of the system. A chemical reaction is an example.

## State Functions

- A *state function* is a property that describes the system and is dependent on the state variables. When a change of state occurs, the change in value of a state function depends only on the initial and final locations of the system, not on the path taken.
- We will study the state function: energy, enthalpy, entropy, and free energy.

## State Functions

Example: How much energy does it take for me to go from the PS lobby to my office on the 6<sup>th</sup> floor?

Path 1: I first take the elevator to my lab on the 8<sup>th</sup> floor to talk to my students, take the stairs to the 7<sup>th</sup> floor to pick up a package from the stockroom, and then take the stairs to my office.

## State Functions

Path 1

$$E = mgh$$

$$\text{step \#1: } h = 29.3 \text{ m; } E = 30.2 \text{ kJ}$$

$$\text{step \#2: } h = -3.66 \text{ m; } E = -3.8 \text{ kJ}$$

$$\text{step \#3: } h = -3.66 \text{ m; } E = -3.8 \text{ kJ}$$

$$\text{total energy} = 30.2 - 3.8 - 3.8 = 22.6 \text{ kJ}$$

## State Functions

Path 2: I stop on the 3<sup>rd</sup> floor to attend a seminar for an hour and then take the elevator directly to the 6<sup>th</sup> floor.

### Path 2

step #1:  $h = 11.0 \text{ m}$ ;  $E = 11.3 \text{ kJ}$

step #2:  $h = 11.0 \text{ m}$ ;  $E = 11.3 \text{ kJ}$

total energy =  $11.3 + 11.3 = 22.6 \text{ kJ}$

Total energy is independent of the path taken.

## Energy

- The energy of a system is perhaps the most important state function to study.
- Energy determines much of the behavior of the system—the desire to be at low energy drives physical and chemical changes.
- A system may contain energy in the form of kinetic energy (the energy of motion) or potential energy (stored energy)

## Energy

- Kinetic energy is the energy associated with a moving object

$$E_k = \frac{1}{2} m v^2$$

m = mass of object; v = velocity

- Potential energy includes the internal energy of molecules and atoms and may be in the form of energy stored in chemical bonds, vibrations of molecules, rotations of molecules, or excitation of electrons in atoms or molecules.

## Energy and Heat

- Energy is exchanged between the system and its surrounding by the transfer of *heat*.
- Remember that temperature is related to the kinetic energy of a system. When heat is exchanged, the kinetic energy of the system changes accompanied by a change in temperature.
- Temperature changes are related to the flow of heat.

## Energy and Heat

- $\Delta T = T_{\text{final}} - T_{\text{initial}} = q/nC$ 
  - q = heat exchanged in process (J)
  - n = number of moles of material (mol)
  - C = heat capacity of material ( $\text{J mol}^{-1} \text{K}^{-1}$ )
- Heat capacity is a measure of a material's ability to accept or give off heat.
- In general, gases have smaller heat capacities than liquids or solids.

## Energy and Heat

- The change in internal energy of a system is related to its heat capacity by the expression:

$$\Delta E = q = n C_v \Delta T$$

where n is the number of moles of material, and  $C_v$  is the heat capacity measured under constant volume conditions.

## Heat Capacity vs Specific Heat

- The heat capacity and specific heat of a compound both measure its ability to accept or give off heat.
- The difference between these two quantities is in the units used:
  - Heat capacity ( $C_v$ ) uses molar units ( $\text{J mol}^{-1} \text{K}^{-1}$ )
  - Specific heat ( $c$ ) uses mass units ( $\text{J g}^{-1} \text{K}^{-1}$ )
- $C_v = c \cdot \text{MW}$  or  $c = C_v / \text{MW}$

## Energy and Heat

### Example

What is the final temperature of a 100. g piece of copper if its energy content is increased by 5.00 kJ and its initial temperature is 298 K?

$$q = n C_v \Delta T$$

$$n_{\text{Cu}} = (100. \text{ g}) / (63.546 \text{ g mol}^{-1}) = 1.57 \text{ mol}$$

$$q = 5.00 \text{ kJ}$$

$$T_f - 298 \text{ K} = (5000 \text{ J}) / (1.57 \text{ mol})(24.435 \text{ J mol}^{-1} \text{K}^{-1})$$

$$T_f - 298 \text{ K} = 130 \text{ K}$$

$$T_f = 428 \text{ K}$$

## Energy and Heat

### Example

If 500. g of iron at 500. K is placed in 1.00 L of water at 298 K, what will be the final temperature of the system when it comes to thermal equilibrium?

$$n_{\text{Fe}} = (500. \text{ g}) / (55.845 \text{ g mol}^{-1}) = 8.95 \text{ mol Fe}$$

$$n_{\text{H}_2\text{O}} = [(1000 \text{ mL})(.9971 \text{ g mL}^{-1})] / [18.015 \text{ g mol}^{-1}] \\ = 55.3 \text{ mol H}_2\text{O}$$

The amount of heat lost by Fe must be equal to the amount of heat gained by H<sub>2</sub>O.

## Energy and Heat

### Example (con't.)

$$q_{\text{Fe}} = -q_{\text{H}_2\text{O}}$$

$$\text{For Fe: } q_{\text{Fe}} = n_{\text{Fe}} C_{\text{Fe}} (T_f - T_i)$$

$$\text{For H}_2\text{O: } q_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}} (T_f - T_i) = -q_{\text{Fe}}$$

Equating, we get:

$$n_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}} (T_f - 298 \text{ K}) = -n_{\text{Fe}} C_{\text{Fe}} (T_f - 500 \text{ K})$$

$$(55.3 \text{ mol})(75.29 \text{ J mol}^{-1}\text{K}^{-1})(T_f - 298 \text{ K}) =$$

$$(8.95 \text{ mol})(25.10 \text{ J mol}^{-1}\text{K}^{-1})(500 \text{ K} - T_f)$$

## Energy and Heat

### Example (con't.)

$$(4160 \text{ J K}^{-1})T_f - 1240 \text{ kJ} = 112 \text{ kJ} - (225 \text{ J K}^{-1})T_f$$

$$(4160 \text{ J K}^{-1} + 225 \text{ J K}^{-1})T_f = 1352 \text{ kJ}$$

$$T_f = (1352 \text{ kJ}) / (4385 \text{ J K}^{-1})$$

$$= 308 \text{ K}$$

## Energy and Work

- The energy of a system may also be used to perform work.

$$w = Fd$$

$$w = \text{work performed (J = kg m}^2 \text{ s}^{-2})$$

$$F = \text{force (N = kg m s}^{-2})$$

$$d = \text{distance (m)}$$

- Work has the same units as energy.

## Energy and Work

- Work is often performed by expansion (or contraction)—the gases produced by combustion in a car's pistons expand, driving the crankshaft; the muscles in our leg contract as we exercise.
- The expansion work of a system is given as:

$$w_{\text{sys}} = -P_{\text{ext}}\Delta V$$

$P_{\text{ext}}$  = external pressure on the system

## Energy and Work

### Example 12-4

A 5.00 cm diameter piston is displaced by 8.00 cm against a pressure of 3.5 atm in an engine. How much work is done by the piston on its surroundings?

$$\begin{aligned}\Delta V &= A(\text{area})d = \pi(2.5 \text{ cm})^2(8.00 \text{ cm}) \\ &= (157 \text{ cm}^3)(1 \text{ m}/100 \text{ cm})^3 = 1.57 \times 10^{-4} \text{ m}^3 \\ w &= -P\Delta V = -(3.5 \text{ atm})(1.57 \times 10^{-4} \text{ m}^3) \\ &= 5.5 \times 10^{-4} \text{ atm m}^3\end{aligned}$$

## Energy and Work

### Example 12-4 (con't.)

$$w = 5.5 \times 10^{-4} \text{ atm m}^3$$

$$1 \text{ atm} = 101300 \text{ Pa} = 101300 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$\begin{aligned} w &= (5.5 \times 10^{-4} \text{ atm m}^3)(101300 \text{ kg m}^{-1} \text{ s}^{-2} \text{ atm}^{-1}) \\ &= 56 \text{ kg m}^2 \text{ s}^{-2} = 56 \text{ J per cylinder stroke} \end{aligned}$$

## 1<sup>st</sup> Law of Thermodynamics

- The 1<sup>st</sup> Law of Thermodynamics is expressed mathematically as:  
$$\Delta E = q + w$$
- If we can measure both the change in heat of the system and the work performed by the system during a change of state, we can calculate the change in internal energy of the system.

## 1<sup>st</sup> Law of Thermodynamics

- The change in energy of the system is equal in magnitude, but opposite in sign, to the change in energy of the surroundings:

$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$$

## Enthalpy

- Enthalpy is a state function closely related to a system's internal energy,  $E$ , but also taking into account the pressure and volume of the system.
- Enthalpy is defined as:

$$H = E + PV$$

## Enthalpy

- The change in enthalpy of a system is given by:

$$\begin{aligned}\Delta H &= \Delta E + \Delta(PV) \\ &= \Delta E + P\Delta V + V\Delta P\end{aligned}$$

## Enthalpy

- For processes occurring under constant pressure conditions, *i.e.*,  $\Delta P = 0$ :

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

$$\Delta E = q_p + w_p = q_p - P\Delta V$$

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

$$\therefore \Delta H = q_p$$

$$\Delta H = C_p\Delta T$$

$C_p$  = constant pressure heat capacity

## Enthalpy

- For chemical changes in which both reactants and products are in the condensed phase (liquid or solid), the volume and pressure of the system does not change significantly, so the  $\Delta(PV)$  term is negligible:

$$\Delta(PV) \approx 0$$

$\Delta H \approx \Delta E$  under condensed phase conditions

## Enthalpy

- For chemical changes involving the reaction or production of gases, we can assume ideal behavior:

$$\Delta(PV) = \Delta(nRT)$$

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

$$= \Delta E + RT\Delta n$$

$\Delta n$  = change in the number of moles of gas during the reaction assuming constant T.

## Heat of Reaction

- When a chemical change occurs, the process may either liberate heat or consume heat.
- The change in heat for the process is called the enthalpy of reaction or the heat of reaction and is given the symbol  $\Delta H_{\text{rxn}}$ .
- For a generic reaction:



## Heat of Reaction

- “Enthalpy of reaction” is the more correct term, but most people still use the phrase “heat of reaction” because many changes in chemistry occur under constant pressure conditions and we showed that:

$$\Delta H = q_p$$



## Heat of Reaction

- The heat of reaction compares the total enthalpy content of the products with the total enthalpy content of the reactants
- If the heat of reaction is positive—the enthalpy of the products is higher than the enthalpy of the reactants—the reaction is called **endothermic**.

Heat must be added to the system in order to get the reaction to occur.



## Heat of Reaction

- If the heat of reaction is negative—the enthalpy of products is lower than the enthalpy of reactants—the reaction is **exothermic**.

The reaction releases heat that may then be used for other purposes.

## Phase Transitions

- Phase transitions occur when the physical state of a compound changes.
- There are three types of phase transitions:
  - Fusion** (melting)—  
solid state → liquid state
  - Vaporization** (boiling)—  
liquid state → gaseous state
  - Sublimation**—  
solid state → gaseous state

## Phase Transitions

- Heat must be put into the system in order for a phase transition to occur
- The heat must come from an external source (fire, hand, sun, etc.)

## Phase Transitions

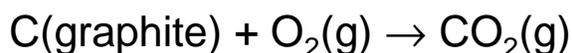
- A phase transition may be represented as a chemical reaction with its accompanying heat of reaction:



- In this case,  $\Delta H_{\text{rxn}}$  is positive meaning we must put energy into the system in order to melt the ice—the reaction is endothermic.
- The reverse process (freezing water) would be exothermic with  $\Delta H_{\text{rxn}} = -6.008 \text{ kJ/mol}$

## Heat of Formation

- The heat of formation of a chemical compound is the enthalpy required to form that compound from its elemental constituents.



$$\Delta H_{\text{f},298}^{\circ} = -393.5 \text{ kJ mol}^{-1}$$

- The  $^{\circ}$  indicates that the reaction occurs at standard pressure of 1 atm making this the standard heat of formation.

## Heat of Formation

### Requirements

- ☞ Reactants are elements in their standard state at the given temperature:  
oxygen at 298 K is  $O_2(g)$ , not  $O(g)$   
mercury at 298 K is  $Hg(l)$   
iron at 298 K is  $Fe(s)$

## Heat of Formation

### Requirements

- ☞ The products, strictly speaking, must also be at the same T as the reactants.
  - ☞ Heats of formation for all elements are zero at any temperature.  
 $\Delta H_f^\circ(F_2) = 0.000... \text{ kJ mol}^{-1}$   
 $\Delta H_f^\circ(Cu) = 0.000... \text{ kJ mol}^{-1}$
- Appendix J lists  $\Delta H_f^\circ$  for some common compounds.

## Heats of Reaction

- If we know the heats of formation for all reactants and products, we can then calculate the heat of reaction:

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma(n\Delta H_{\text{f}}^{\circ})_{\text{prod}} - \Sigma(n\Delta H_{\text{f}}^{\circ})_{\text{react}}$$

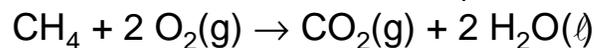
$n$  = stoichiometric coefficient of reactant or product

This is called *Hess's Law*—"products minus reactants"

## Heats of Reaction

### Example

Combustion of methane,  $\text{CH}_4$



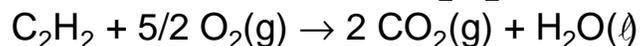
$$\Delta H_{\text{f}}^{\circ} \quad -74.8 \quad 0.0 \quad -393.5 \quad -285.8$$

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= [(-393.5 \text{ kJ mol}^{-1}) + 2 \cdot (-285.8 \text{ kJ mol}^{-1})] \\ &\quad - [(-74.8 \text{ kJ mol}^{-1}) + 2 \cdot (0.0 \text{ kJ mol}^{-1})] \\ &= -890.3 \text{ kJ mol}^{-1} \end{aligned}$$

## Heats of Reaction

### Example

Combustion of acetylene,  $C_2H_2$



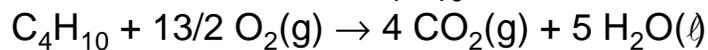
$$\Delta H_f^\circ \quad 227.4 \quad 0.0 \quad -393.5 \quad -285.8$$

$$\begin{aligned} \Delta H_{rxn}^\circ &= [2 \cdot (-393.5 \text{ kJ mol}^{-1}) + (-285.8 \text{ kJ mol}^{-1})] \\ &\quad - [(227.4 \text{ kJ mol}^{-1}) + 2.5 \cdot (0.0 \text{ kJ mol}^{-1})] \\ &= -1300.2 \text{ kJ mol}^{-1} \end{aligned}$$

## Heats of Reaction

### Example

Combustion of butane,  $C_4H_{10}$



$$\Delta H_f^\circ \quad -124.7 \quad 0.0 \quad -393.5 \quad -285.8$$

$$\begin{aligned} \Delta H_{rxn}^\circ &= [4 \cdot (-393.5 \text{ kJ mol}^{-1}) + 5 \cdot (-285.8 \text{ kJ mol}^{-1})] \\ &\quad - [(-124.7 \text{ kJ mol}^{-1}) + 6.5 \cdot (0.0 \text{ kJ mol}^{-1})] \\ &= -2878.3 \text{ kJ mol}^{-1} \end{aligned}$$

## Specific Types of Heats of Reaction

- Heat of Solution—the energy released when a solute is dissolved into solution.

$$\Delta H_{\text{soln}}(\text{CaCl}_2) = -81.8 \text{ kJ mol}^{-1}$$

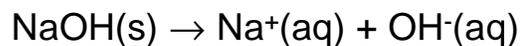
$$\Delta H_{\text{soln}}(\text{NaCl}) = +3.8 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{soln}}(\text{H}_2\text{SO}_4) = -73.4 \text{ kJ mol}^{-1}$$

## Heat of Solution

### Example

Dissolution of sodium hydroxide, NaOH(s)



$$\Delta H^{\circ}_{\text{f}} \quad -425.6 \quad -240.3 \quad -230.0$$

$$\begin{aligned} \Delta H^{\circ}_{\text{rxn}} &= [(-240.3 \text{ kJ mol}^{-1}) + (-230.0 \text{ kJ mol}^{-1})] \\ &\quad - (-425.6 \text{ kJ mol}^{-1}) \\ &= -44.7 \text{ kJ mol}^{-1} \end{aligned}$$

## Specific Types of Heats of Reaction

- Heat of Vaporization—the energy that must be put into a system in order to get a substance to boil.

$$\Delta H_{\text{vap}}(\text{CH}_3\text{OH}) = +39.2 \text{ kJ mol}^{-1}$$

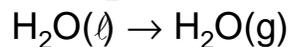
$$\Delta H_{\text{vap}}(\text{C}_2\text{H}_5\text{OH}) = +40.5 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{vap}}(\text{C}_3\text{H}_7\text{OH}) = +47.3 \text{ kJ mol}^{-1}$$

## Specific Types of Heats of Reaction

### Example

Vaporization of  $\text{H}_2\text{O}$



$$\Delta H_{\text{f},298}^{\circ} \quad -285.83 \quad -241.83$$

$$\begin{aligned} \Delta H_{\text{vap}}^{\circ} &= -241.83 \text{ kJ mol}^{-1} - (-285.83 \text{ kJ mol}^{-1}) \\ &= 44.00 \text{ kJ mol}^{-1} \end{aligned}$$

Literature value is  $40.79 \text{ kJ mol}^{-1}$ —why is there a difference?

The  $\Delta H_{\text{f}}^{\circ}$  above are given at 298 K, not 373 K where  $\text{H}_2\text{O}$  boils. Values of  $\Delta H_{\text{f}}^{\circ}$  change with T.

## Specific Types of Heats of Reaction

- Heat of Fusion—the energy that must be put into a system in order to get a substance to melt.

$$\Delta H_{\text{fus}}(\text{CH}_3\text{OH}) = +3.18 \text{ kJ mol}^{-1}$$

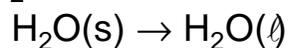
$$\Delta H_{\text{fus}}(\text{C}_2\text{H}_5\text{OH}) = +5.02 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{fus}}(\text{C}_3\text{H}_7\text{OH}) = +5.19 \text{ kJ mol}^{-1}$$

## Specific Types of Heats of Reaction

### Example

Fusion of  $\text{H}_2\text{O}$



$$\Delta H_{\text{f}}^{\circ} \quad -293.72 \quad -287.71$$

$$\begin{aligned} \Delta H_{\text{fus}}^{\circ} &= -287.71 \text{ kJ mol}^{-1} - (-293.72 \text{ kJ mol}^{-1}) \\ &= 6.01 \text{ kJ mol}^{-1} \end{aligned}$$

## Specific Types of Heats of Reaction

- Heat of Sublimation—the energy that must be put into a system in order to get a substance to go from solid to vapor phase.

$$\Delta H_{\text{subl}}(\text{CO}_2) = +25.2 \text{ kJ mol}^{-1}$$

## Specific Types of Heats of Reaction

### Example

A beaker weighing 260.0 g at 298 K contains 32.8 mL of acetone ( $\text{C}_3\text{H}_6\text{O}$ ). If all of the acetone evaporates, what is the final temperature of the beaker?

$$\rho(\text{acetone}) = 0.7899 \text{ g mL}^{-1}$$

$$\Delta H_{\text{vap}}(\text{acetone}) = 31.97 \text{ kJ mol}^{-1}$$

$$\text{MM}(\text{acetone}) = 58.079 \text{ g mol}^{-1}$$

$$C_p(\text{SiO}_2) = 44.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

## Specific Types of Heats of Reaction

### Example (con't.)

$$m(\text{acetone}) = (32.8 \text{ mL})(0.7899 \text{ g mL}^{-1}) = 25.9 \text{ g}$$

$$(25.9 \text{ g})/(58.079 \text{ g mol}^{-1}) = 0.446 \text{ mol acetone}$$

heat required to vaporize acetone:

$$q = (0.446 \text{ mol})(31.97 \text{ kJ mol}^{-1}) = 14.3 \text{ kJ}$$

This heat must come from the beaker.

$$q = nC_p\Delta T = nC_p(T_f - T_i)$$

$$-14300 \text{ J} = (4.33 \text{ mol})(44.4 \text{ J mol}^{-1} \text{ K}^{-1})(T_f - 298 \text{ K})$$

$$T_f = 224 \text{ K}$$

## Molar Quantities

- The thermodynamic state functions are usually reported as molar quantities, *i.e.*, the enthalpy change of reaction for a mole of material.

$$\Delta E_{\text{molar}} = \Delta E/n \quad \text{units} = \text{J mol}^{-1}$$

$$\Delta H_{\text{molar}} = \Delta H/n \quad \text{units} = \text{J mol}^{-1}$$

- Unless otherwise stated, you can assume that quantities in this section are molar quantities.

## Practice Problems

A 15.0 g piece of silver is immersed in 25.0 g of water. The system is heated from 24.0 °C to 37.6 °C. How many joules of energy are absorbed by the silver and by the water?

$$\text{Ag: } (15.0 \text{ g}) / (107.87 \text{ g mol}^{-1}) = .139 \text{ mol Ag}$$

$$C_p(\text{Ag}) = 25.351 \text{ J mol}^{-1}\text{K}^{-1}$$

$$q = nC\Delta T$$

$$= (.139 \text{ mol})(25.351 \text{ J mol}^{-1}\text{K}^{-1})(310.8 \text{ K} - 297.2 \text{ K})$$

$$= 47.9 \text{ J of energy to Ag}$$

$$\text{H}_2\text{O: } (25.0 \text{ g}) / (18.01 \text{ g mol}^{-1}) = 1.39 \text{ mol H}_2\text{O}$$

$$C_p(\text{H}_2\text{O}) = 75.291 \text{ J mol}^{-1}\text{K}^{-1}$$

$$q = (1.39 \text{ mol})(75.291 \text{ J mol}^{-1}\text{K}^{-1})(310.8 \text{ K} - 297.2 \text{ K})$$

$$= 1420 \text{ J energy to H}_2\text{O}$$

## Practice Problems

How much work is done when blowing up a balloon from no volume to 2.5 L, assuming  $P_{\text{ext}} = 1.00 \text{ atm}$  and that no work is required to stretch the rubber.

$$w = -P_{\text{ext}}\Delta V$$

$$= -(1.00 \text{ atm})(2.5 \text{ L} - 0.0 \text{ L}) = -2.5 \text{ L atm}$$

$$w = (-2.5 \text{ L atm}) \left( \frac{101325 \text{ N m}^{-2}}{1 \text{ atm}} \right) \left( \frac{1 \text{ m}^3}{1000 \text{ L}} \right) = -250 \text{ J of work}$$

## Practice Problems

An electric heater adds 19.75 kJ heat to a constant volume calorimeter and the temperature increases by 4.22 K. When 1.75 g methanol is burned, the temperature increases by 8.47 K. Calculate the molar heat of combustion of methanol.

Step I: determine C of calorimeter

$$C = q/\Delta T = (19750 \text{ J})/(4.22 \text{ K}) = 4680 \text{ J K}^{-1}$$

Step II: determine q released by combustion of CH<sub>3</sub>OH

$$q = C\Delta T = (4680 \text{ J K}^{-1})(8.47 \text{ K}) = 39.6 \text{ kJ of heat}$$

Step III: calculate molar heat of combustion

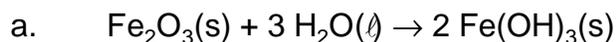
$$(1.75 \text{ g})/(32.04 \text{ g mol}^{-1}) = .0546 \text{ mol CH}_3\text{OH}$$

$$(39.6 \text{ kJ})/(.0546 \text{ mol}) = 725 \text{ kJ mol}^{-1} \text{ (lit} = 726 \text{ kJ mol}^{-1}\text{)}$$

Since CH<sub>3</sub>OH is a liquid,  $\Delta E_{\text{rxn}} \approx \Delta H_{\text{rxn}}$

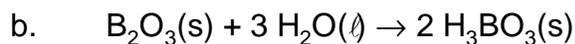
## Practice Problems

Determine heats of reaction for the following using standard heats of formation:



$$\Delta H_{\text{f}}^{\circ} \quad -824.2 \quad -285.83 \quad -823.0$$

$$\Delta H_{\text{rxn}}^{\circ} = [2(-823.0)] - [-824.2 - 3(-285.83)] = +35.7 \text{ kJ mol}^{-1}$$



$$\Delta H_{\text{f}}^{\circ} \quad -1273.5 \quad -285.83 \quad -1094.3$$

$$\Delta H_{\text{rxn}}^{\circ} = [2(-1094.3)] - [(-1273.5) - 3(-285.83)] \\ = -57.6 \text{ kJ mol}^{-1}$$

## Practice Problems

A 7.65 g cold coin is heated to 100.0 °C in boiling water. The coin is then quickly placed in an ice calorimeter. What mass of ice melts?

$$\text{Au: } (7.65 \text{ g}) / (196.97 \text{ g mol}^{-1}) = .0388 \text{ mol Au}$$

$$C_p(\text{Au}) = 25.418 \text{ J mol}^{-1}\text{K}^{-1}$$

Step I: determine heat lost by gold when going from 100.0 °C to 0.0 °C

$$q = nC_p\Delta T = (.0388 \text{ mol})(25.418 \text{ J mol}^{-1}\text{K}^{-1})(-100 \text{ K}) \\ = -98.6 \text{ J of heat}$$

Step II: determine how much ice melts

$$\Delta H_{\text{fus}}^{\circ}(\text{H}_2\text{O}) = 6.01 \text{ kJ mol}^{-1}$$

$$n = q / \Delta H_{\text{fus}}^{\circ} = (98.6 \text{ J}) / (6010 \text{ J mol}^{-1}) = .0164 \text{ mol H}_2\text{O}$$

$$(.0164 \text{ mol})(18.01 \text{ g mol}^{-1}) = .295 \text{ g H}_2\text{O melted}$$