Chemistry Green

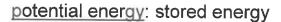
Week 3 & 4

Energy

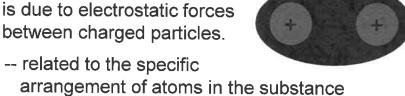
kinetic energy: energy of motion;

- -- all particles have KE
- -- Thermal energy is due to the KE of particles.

We measure the average KE of a collection of particles as...temperature.



Chemical potential energy is due to electrostatic forces



SI unit Units of energy are joules (J), * kilojoules (kJ), calories (cal), or nutritional calories (Cal or kcal).



James Prescott Joule (1818-1889)

-- conversions:

4184 J = 4.184 kJ = 1000 cal = 1 Cal = 1 kcal

system: the part of the universe we are studying

surroundings: everything else

In chemistry, a
 <u>closed system</u>
 can exchange energy
 but not matter with
 its surroundings.

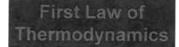


- -- Usually, energy is transferred to...
 - ...(1) change an object's state of motion
 - ...or...(2) cause a temperature change

Work (w) is done when a force moves through a distance. W = F d

Heat (q) is an amount of energy transferred from a hotter object to a colder one.

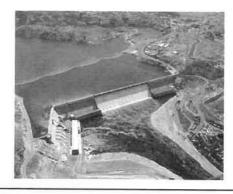
Find the kinetic energy of a single dinitrogen monoxide molecule moving at 650 m/s. N_2O (laughing gas) $KE = \frac{1}{2} \text{ mv}^2$ m = 44 armu $\frac{1 \text{ g}}{6.02 \times 10^{23} \text{ armu}}$ $\frac{1 \text{ kg}}{1000 \text{ g}}$ $= 7.31 \times 10^{-26} \text{ kg}$ $KE = \frac{1}{2} (7.31 \times 10^{-26} \text{ kg}) (650 \text{ m/s})^2$ $= 1.5 \times 10^{-20} \text{ J}$

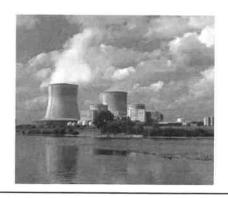


Law of Conservation of Energy

-- Energy morphs between its various forms, but the total amount remains the same.

(pretty much)





internal energy (E) of a system: the sum of <u>all</u> the KE and PE of the components of a system (this is **impossible** for us to know)

-- The change in the internal energy of a system would be found by: $\Delta E = E_{final} - E_{initial}$

And for chemistry, this equation would become:

$$\Delta E = E_{products} - E_{reactants}$$

 ΔE is + if E_{final} > $E_{initial}$ (i.e., system... gains energy)

→ ENDOTHERMIC

 ΔE is – if E_{final} < $E_{initial}$ (i.e., system... loses energy)

→ EXOTHERMIC

But we ARE able to find ΔE by measuring two types of "energy" quantities:

$$\Delta E = q + w$$

q = heat: +/- q = system absorbs/releases heat

w = work: +/- w = work done <u>on/by</u> system

** KEY: Sign conventions are based on the system's point of view.

The *Titanic* was propelled by massive steam engines. The internal energy of the water molecules of the steam changed from instant to instant, depending on how much heat they were absorbing and how much work they were doing during a given time interval.



In <u>endothermic</u> processes, heat is <u>absorbed</u> by the system.

e.g., melting boiling sublimation



In <u>exothermic</u> processes, heat is <u>released</u> by the system.

e.g., freezing condensation deposition



To go further, we must introduce the concept of enthalpy (H).

-- Enthalpy (H) is defined as... H = E + PV

where

E = system's internal energy

P = pressure of the system

V = volume of the system



Heike Kamerlingh Onnes 1853–1926

The Dutch physicist and Nobel laureate H.K. Onnes coined the term *enthalpy*, basing it on the Greek term *enthalpein*, which means "to warm."

-- There is much that could be said about enthalpy, but what you need to know is:

If a process occurs at constant pressure, the change in enthalpy of the system equals the heat lost or gained by the system.

i.e.,

P indicates constant pressure conditions.

When ΔH is +, the system... has gained heat. (ENDO) When ΔH is –, the system... has lost heat. (EXO) Enthalpy is an extensive property, meaning that...

the amount of material affects its value.

<u>enthalpy</u> of reaction:

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

(also called "heat of reaction")

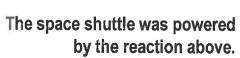
For exothermic rxns, the <u>heat content</u> of the reactants is than that of the products.

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$$
 $\Delta H = -483.6 \text{ kJ}$

What is the enthalpy change when 178 g of H₂O are produced?

$$178 \text{ g-H}_2Q \left(\frac{1 \text{ molH}_2Q}{18 \text{ gH}_2Q} \right) \left(\frac{483.6 \text{ kJ}}{2 \text{ molH}_2Q} \right)$$

 $\Delta H = -2390 \text{ kJ}$





 ΔH for a reaction and its reverse are the opposites of each other.

Enthalpy/energy is a reactant.

$$2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(g)$$
 ($\Delta H =$

$$2 H_2O(g) \longrightarrow 2 H_2(g) + O_2(g)$$
 ($\Delta H =$

Enthalpy change depends on the states of reactants and products.

$$2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(g) \quad (\Delta H = -483.6 \text{ kJ})$$

$$2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(l)$$

Calorimetry: the measurement of heat flow

-- device used is called a... calorimeter

heat capacity of an object: amount of heat needed to raise object's temp. 1 K = 1°C

molar heat capacity: amt. of heat needed to raise temp. of 1 mol of a substance 1 K

specific heat (capacity): amt. of heat needed to raise temp. of 1 g of a substance 1 K

i.e.,

molar heat capacity = molar mass X specific heat

We calculate the heat a substance loses or gains using:

$$q = \underline{m} c_P \Delta T$$

AND

$$q = +/\underline{m} c_X$$

(for within a given state of matter)

(for <u>between</u> two states of matter)

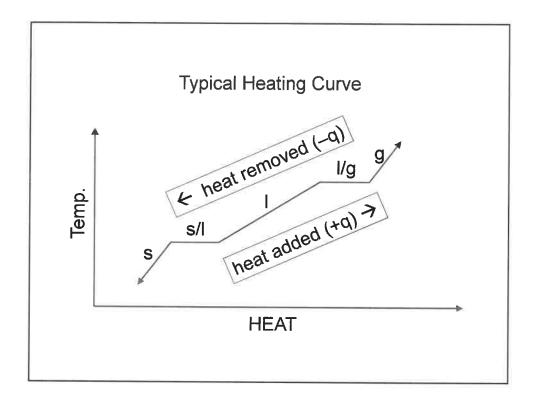
where q = heat

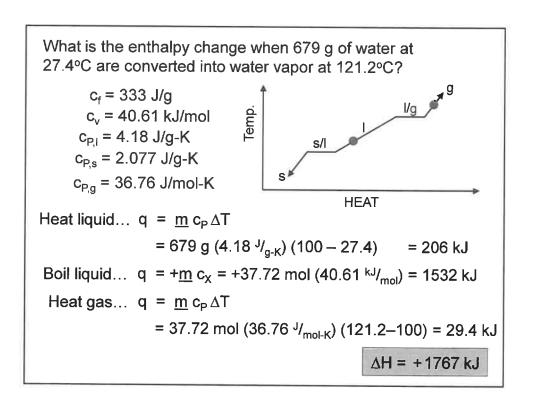
m = amount of substance

c_P = substance's heat capacity

 ΔT = temperature change

c_X = heat of fusion (s/l) or heat of vaporization (l/g)





With a <u>coffee-cup calorimeter</u>, a reaction is carried out under constant pressure conditions.

- -- Why is the pressure constant?calorimeter isn't sealed,atmospheric pressure is constant
- -- If we assume that no heat is exchanged between the system and the surroundings, then the solution must absorb any heat given off by the reaction.

i.e.,
$$q_{absorbed} = -q_{released}$$

the specific heat of water

-- For dilute aqueous solutions, it is a safe assumption that $c_P = 4.18 \text{ J/g-K}$

When 50.0 mL of 0.100 M AgNO₃ and 50.0 mL of 0.100 M HCl are mixed in a coffee-cup calorimeter, the mixture's temperature increases from 22.30°C to 23.11°C. Calculate the enthalpy change for the reaction, per mole of AgNO₃.

AgNO₃ + HCl
$$\rightarrow$$
 AgCl + HNO₃

Assume:

-- mixture $c_P = c_P$ of H₂O

-- mixture mass = 100 g

0.05 L, 0.05 L, 0.1 M 0.1 M 0.005 mol 0.005 mol

$$\Delta H = \frac{338.58 \text{ J}}{0.005 \text{ mol AgNO}_3}$$

$$q = \underline{m} c_P \Delta T$$

$$-67.7 \frac{kJ}{\text{mol AgNO}_3}$$

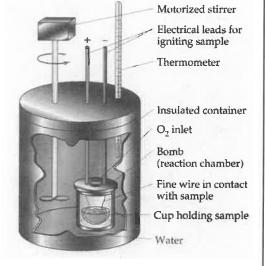
 $= 338.58 \text{ J (for } 0.005 \text{ mol AgNO}_3)$

Combustion reactions are studied using constant-volume calorimetry.

This technique requires a bomb calorimeter.

 The heat capacity of the bomb calorimeter (C_{cal}) must be known.

unit is J/K (or the equivalent)



bomb calorimeter

-- Again, we assume that no energy escapes into the surroundings, so that the heat absorbed by the bomb calorimeter equals the heat given off by the reaction.

Solve bomb calorimeter problems by unit cancellation.



another bomb calorimeter

A 0.343-g sample of propane, C_3H_8 , is burned in a bomb calorimeter with a heat capacity of 3.75 kJ/°C. The temperature of the material in the calorimeter increases from 23.22°C to 27.83°C. Calculate the molar heat of combustion of propane.



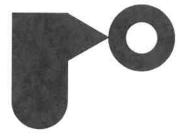
$$3.75 \frac{kJ}{^{\circ}C} (27.83^{\circ}C-23.22^{\circ}C)$$

$$\frac{17.29 \text{ kJ}}{0.343 \text{ gr}} \left(\frac{44 \text{ gr}}{1 \text{mol C}_3 \text{H}_8} \right)$$

-2220 kJ/mol

Hess's Law

The ΔH_{rxn} s have been calculated and tabulated for many basic reactions. Hess's law allows us to put these simple reactions together like puzzle pieces such that they add up to a more complicated reaction that we are interested in. By adding or subtracting the ΔH_{rxn} s as appropriate, we can determine the ΔH_{rxn} of the more complicated reaction.



The area of a composite shape can be found by adding/subtracting the areas of simpler shapes.

Calculate the heat of reaction for the combustion of sulfur to form sulfur dioxide.

$$2 SO_2(g) + O_2(g) \longrightarrow 2 SO_3(g)$$
 ($\Delta H = -198.2 \text{ kJ}$)

$$S_8(s) + 12 O_2(g) \rightarrow 8 SO_3(g) \quad (\Delta H = -3161.6 \text{ kJ})$$

$$(S_8(s)) + 8 O_2(g) \rightarrow 8 SO_2(g)$$
 (TARGET)

$$(S_8(s)) + 12 O_2(g) \rightarrow (8 SO_3(g)) \quad (\Delta H = -3161.6 \text{ kJ})$$

$$(2 \text{ SO}_2(g) + O_2(g) \rightarrow 2 \text{ SO}_3(g) (\Delta H = -198.2 \text{ kJ})$$

$$S_8(s) + 8 O_2(g) \rightarrow 8 SO_2(g) \stackrel{\text{defed}}{\longrightarrow} 12 + 2 \stackrel{\text{defed}}{$$

Calculate ΔH for the reaction... 5 C + 6 H₂ \longrightarrow C₅H₁₂ given the following:

$$C_5H_{12} + 8 O_2 \rightarrow 5 CO_2 + 6 H_2O (\Delta H = -3535.6 kJ)$$

$$C + O_2 \longrightarrow CO_2$$
 $(\Delta H = -393.5 \text{ kJ})$
 $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ $(\Delta H = -285.8 \text{ kJ})$

$$(\Delta H = -393.5 \text{ kJ})$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

$$(\Delta H = -285.8 \text{ kJ})$$

$$6.6Q_2 + 8.0Q_2 + 5.0Q_{12} + 6.0Q_2 (\Delta H = +3535.6 kJ)$$

$$5 \text{ C} + 5 \text{ G}_2 \longrightarrow 5 \text{ GO}_2 \quad (\Delta H = -396.55 \text{ keV})$$

$$6 \text{ Hz} + 285488 \text{ Hz}$$
 ($\Delta H = -285488 \text{ Hz}$)

$$5 \text{ C} + 6 \text{ H}_2 \rightarrow \text{ C}_5 \text{H}_{12}$$
 $\Delta H = -146.7 \text{ kJ}$

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 $C + O_2 \longrightarrow CO_2 \ (\Delta H = -393.5 \text{ kJ})$
 $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O \ (\Delta H = -285.8 \text{ kJ})$

enthalpy of formation (ΔH_f): the enthalpy change associated with the formation of a compound from its constituent elements

-- also called....

When finding the <u>standard enthalpy of formation</u> (ΔH_f^o), all substances must be in their standard states. The "standard state" of a substance has arbitrarily been chosen to be the state of the substance at 25°C

(298 K). If more than one form of the element exists at 298 K, then the standard state is the most stable form,



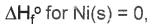
e.g.,

-- By definition, ΔH_f^o for the most stable form of any element in its standard state is zero.

e.g., ΔH_f^o for $O_2(g)$ or Al(s) or $S_8(s)$, etc. is ZERO

- -- ΔH_f values are for 1 mol of substance, so the units are typically kJ/mol.
- Many ∆H_f values have been tabulated.







but is $\neq 0$ for Fe₂O₃.

standard enthalpy of a reaction (ΔH°_{rxn}):

 ΔH^{o}_{rxn} is the change in enthalpy of a reaction when all substances are in their standard states (i.e., at 25°C).

-- Using Hess's law, we can easily calculate ΔH°_{rxn} from the ΔH_{f}° of all R and P.



Germain Henri Hess (1802 – 1850)

-- equation:

 $\Delta H^{o}_{rxn} = \Sigma n \ \Delta H^{o}_{f}(products) - \Sigma m \ \Delta H^{o}_{f}(reactants)$

where n and m are the coefficients in the balanced equation

Approximate the enthalpy change for the combustion of 246 g of liquid methanol.

2 CH₃OH(I) + 3 O₂(g)
$$\longrightarrow$$
 2 CO₂(g) + 4 H₂O(g)

-238.6 kJ/_{mol} 0 kJ/_{mol} -393.5 kJ/_{mol} -241.8 kJ/_{mol} X 2 X 4

-477.2 kJ -1754.2 kJ

$$\Delta H^o_{rxn} = -1754.2 \text{ kJ} - (-477.2 \text{ kJ}) = -1277 \text{ kJ}$$
So...
$$\frac{-1277 \text{ kJ}}{64 \text{ g}} = \frac{\text{X kJ}}{246 \text{ g}}$$
for 2 mol (i.e., 64 g) of CH₃OH

Hess's Law Worksheet

1. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(g)$$
 $\Delta H = -2439 \text{ kJ}$
 $4PCl_5(g) \rightarrow P_4(s) + 10Cl_2(g)$ $\Delta H = 3438 \text{ kJ}$

2. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $2CO_2(g) + H_2O(g) \rightarrow C_2H_2(g) + 5/2O_2(g)$

$$\begin{array}{lll} C_2H_2(g) + 2H_2(g) & \to & C_2H_6(g) & \Delta H = -94.5 \text{ kJ} \\ H_2O(g) & \to & H_2(g) + 1/2O_2(g) & \Delta H = 71.2 \text{ kJ} \\ C_2H_6(g) + 7/2O_2(g) & \to & 2CO_2(g) + 3H_2O(g) & \Delta H = -283 \text{ kJ} \end{array}$$

3. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $N_2H_4(l)~+~H_2(g)~\to~2NH_3(g)$

$$\begin{array}{lll} N_2H_4(l) \, + \, CH_4O(l) \, \to \, CH_2O(g) \, + \, N_2(g) \, + \, 3H_2\,(g) & \Delta H = -37 \; kJ \\ N_2(g) \, + \, 3H_2(g) \, \to \, 2NH_3(g) & \Delta H = -46 \; kJ \\ CH_4O(l) \, \to \, CH_2O(g) \, + \, H_2(g) & \Delta H = -65 \; kJ \end{array}$$

4. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $H_2SO_4(l) \rightarrow SO_3(g) + H_2O(g)$

$$\begin{array}{ll} H_2S(g) \ + \ 2O_2(g) \ \to \ H_2SO_4(l) & \Delta H = -235.5 \ kJ \\ H_2S(g) \ + \ 2O_2(g) \ \to \ SO_3(g) \ + \ H_2O(l) & \Delta H = -207 \ kJ \\ H_2O(l) \ \to \ H_2O(g) & \Delta H = 44 \ kJ \end{array}$$

5. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $2C_2H_4O(l)+2H_2O(l)\rightarrow 2C_2H_6O(l)+O_2(g)$

$$\begin{array}{ll} C_2H_6O(l) \ + \ 3O_2(g) \ \rightarrow \ 2CO_2(g) \ + \ 3H_2O(l) & \Delta H = -685.5 \ kJ \\ C_2H_4O(l) \ + \ 5/2O_2(g) \ \rightarrow \ 2CO_2(g) \ + \ 2H_2O(l) & \Delta H = -583.5 \ kJ \\ \end{array}$$

6. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
 $\Delta H = -115 \text{ kJ}$
 $2NH_3(g) + 4H_2O(l) \rightarrow 2NO_2(g) + 7H_2(g)$ $\Delta H = -142.5 \text{ kJ}$
 $H_2O(l) \rightarrow H_2(g) + 1/2O_2(g)$ $\Delta H = -43.7 \text{ kJ}$

7. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $CO_2(g) \rightarrow C(s) + O_2(g)$

$$H_2O(1) \rightarrow H_2(g) + 1/2O_2(g)$$
 $\Delta H = 643 \text{ kJ}$ $C_2H_6(g) \rightarrow 2C(s) + 3H_2(g)$ $\Delta H = 190.6 \text{ kJ}$ $2CO_2(g) + 3H_2O(1) \rightarrow C_2H_6(g) + 7/2O_2(g)$ $\Delta H = 3511.1 \text{ kJ}$

8. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $N_2H_4(l) + CH_4O(l) \rightarrow CH_2O(g) + N_2(g) + 3H_2(g)$

$$\begin{array}{lll} 2NH_3(g) \ \to \ N_2H_4(l) \ + \ H_2(g) & \Delta H = 22.5 \ kJ \\ 2NH_3(g) \ \to \ N_2(g) \ + \ 3H_2(g) & \Delta H = 57.5 \ kJ \\ CH_2O(g) \ + \ H_2(g) \ \to \ CH_4O(l) & \Delta H = 81.2 \ kJ \end{array}$$

9. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $1/2H_2(g) + 1/2Cl_2(g) \rightarrow HCl(g)$

$$\begin{array}{lll} COCl_{2}(g) \ + \ H_{2}O(l) \ \to \ CH_{2}Cl_{2}(l) \ + \ O_{2}(g) & \Delta H = 47.5 \ kJ \\ 2HCl(g) \ + \ 1/2O_{2}(g) \ \to \ H_{2} \ O(l) \ + \ Cl_{2}(g) & \Delta H = 105 \ kJ \\ CH_{2}Cl_{2}(l) \ + \ H_{2}(g) \ + \ 3/2O_{2}(g) \ \to \ COCl_{2}(g) \ + \ 2H_{2}O(l) & \Delta H = -402.5 \ kJ \\ \end{array}$$

10. Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $C_2H_2(g)+5/2O_2(g)\rightarrow 2CO_2(g)+H_2O(g)$

$$C_2H_6(g) \rightarrow C_2H_2(g) + 2H_2(g)$$
 $\Delta H = 283.5 \text{ kJ}$ $H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$ $\Delta H = -213.7 \text{ kJ}$ $2CO_2(g) + 3H_2O(g) \rightarrow C_2H_6(g) + 7/2O_2(g)$ $\Delta H = 849 \text{ kJ}$

(12) Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values: $Zn(s) + 1/8S_8(s) + 2O_2(g) \rightarrow ZnSO_4(s)$

$$\begin{array}{lll} Zn(s) + 1/8S_8(s) & \to & ZnS(s) & \Delta H = -183.92 \ kJ \\ 2ZnS(s) + 3O_2(g) & \to & 2ZnO(s) + 2SO_2(g) & \Delta H = -927.54 \ kJ \\ 2SO_2(g) + O_2(g) & \to & 2SO_3(g) & \Delta H = -196.04 \ kJ \\ ZnO(s) + SO_3(g) & \to & ZnSO_4(s) & \Delta H = -230.32 \ kJ \\ Answer = -976.03 \ kJ & \Delta H = -230.32 \ kJ \end{array}$$

These problems involve using heat of formation values that are found in the appendix of your textbook.

(13) What is the enthalpy of the following reactions?

(a)
$$SiF_4(g) \rightarrow Si(s) + 2F_2(g)$$
 (answer: +1615.0 kJ)

(b)
$$SiF_4(g) \rightarrow Si(g) + 2F_2(g)$$
 (answer: +2065.0 kJ)

(c)
$$SO_3(g) + H_2O(g) \rightarrow H_2SO_4(aq)$$
 (answer: -271.8 kJ)

(d)
$$3K_2O_2(s) + 3H_2O(l) \rightarrow 6KOH(aq) + O_3(g)$$
 (answer: -412 kJ) (not -411.7 kJ)

(e)
$$Fe_3O_4(s) + 8HCl(g) \rightarrow 2FeCl_3(s) + FeCl_2(s) + 4H_2O(g)$$
 (answer: -252 kJ) (not -251.6 kJ)

Calorimetry WS

1. Calculate the kinetic energy of a molecule of sulfur trioxide moving at 470 m/s.

2. How fast would a dinitrogen pentoxide molecule be moving if it had 7.1 x 10-20 J of kinetic energy?

For Question 3, find the change in internal energy, and state whether the process is endothermic or exothermic.

- 3A. A system does 156 J of work on the surroundings and absorbs 76 J of heat.
- 3B. A system has 4.67 kJ of work done on it and absorbs 1,263 J of heat.
- 4. The complete combustion of what mass of octane will yield 8,260 kJ of energy?

$$2 C_8H_{18} + 25 O_2 \rightarrow 16 CO_2 + 18 H_2O$$
 $\Delta H = -11,020 \text{ kJ}$

5. If the heat of combustion of 1-butanol (C₄H₉OH) is 2,710 kJ/mol, what mass of oxygen is consumed when enough 1-butanol is burned to yield 26,400 kJ of energy?

For Question 6, any or all of the following calorimetry values for water may prove u	seful:
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$$c_{p,l}$$
 = 4.18 J/g-K, $c_{p,s}$ = 2.077 J/g-K, $c_{p,g}$ = 36.76 J/mol-K, c_f = 333 J/g, c_v = 40.61 kJ/mol

6A. Find the change in enthalpy required to change 140 g of 78°C water into -24°C ice.

6B. Find the change in enthalpy required to change 260 g of -14°C ice into 135°C superheated steam.

7. If a 34.5 g mass of 375.0°C iron is placed in 50.0 g of 18.5°C water, what is the final temperature of the system? Iron's specific heat is 0.449 J/g-K.

8. If a 64.1 g block of 315.0°C aluminum is placed in 80.0 g of 16.0°C water, what is the final temperature of the system? Aluminum's specific heat is 0.890 J/g-K.

ANSWERS: 6A. –99 kJ 6B. +810 kJ 7. 43.1°C 8. 59.6°C