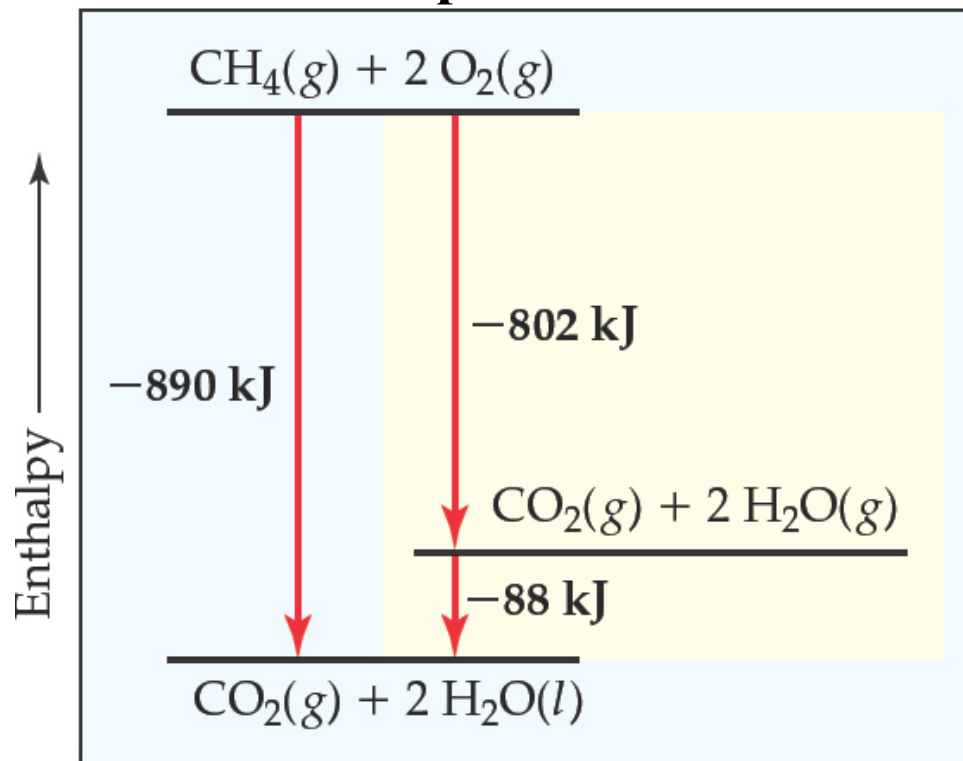# Hess's Law

- **Hess's law: If a reaction is carried out in a series of steps, ΔH for the overall reaction equals the sum of the enthalpy changes for the individual steps.**

- **Because H is a state function, for a particular set of reactants and products, ΔH is the same whether the reaction takes place in one step or in a series of steps.**

Hess's Law

If a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the individual steps.

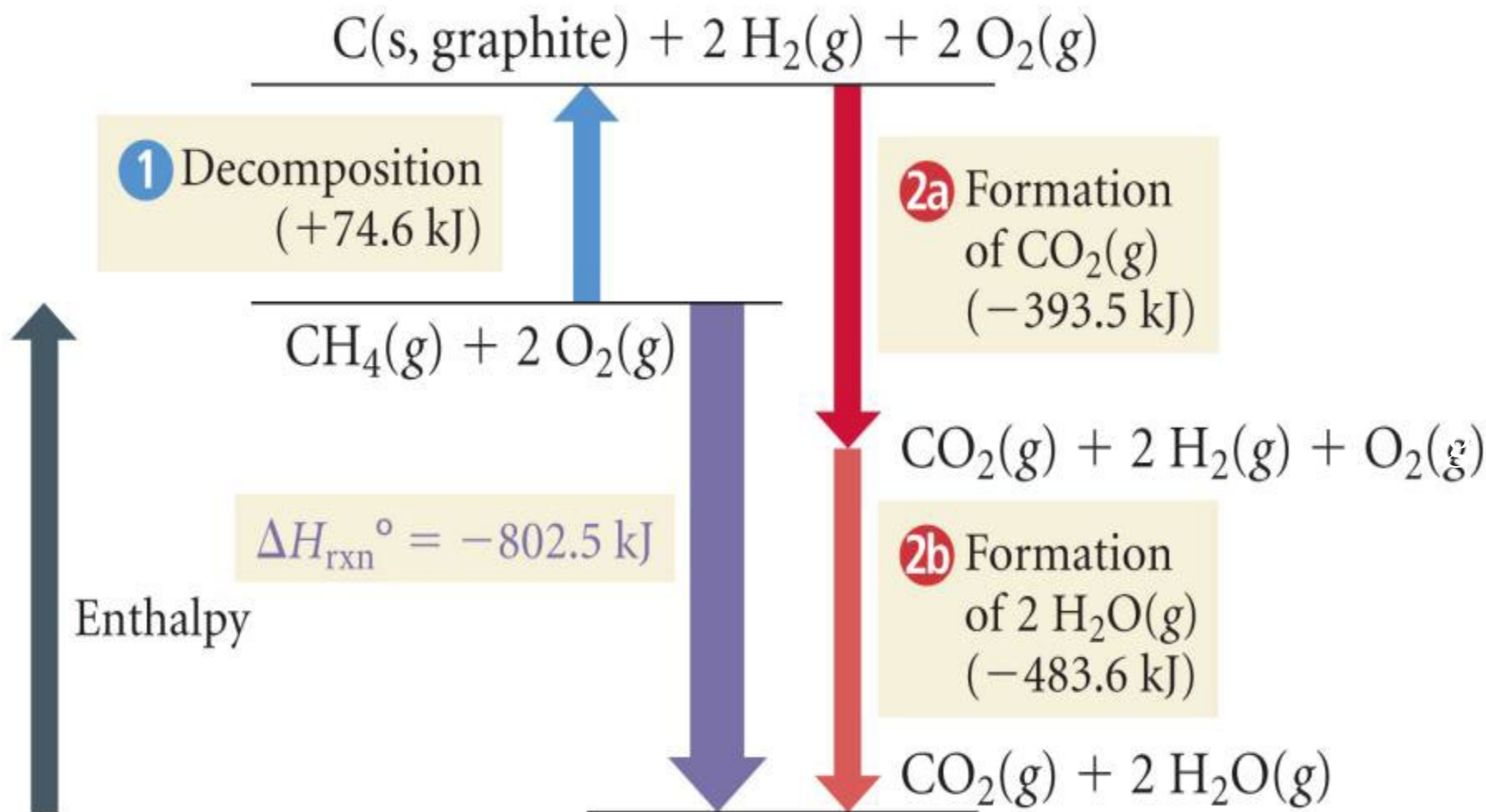**For example, consider the reaction of tin and chlorine:**

$$Sn(s) + Cl_2(g) \rightarrow SnCl_2(s) \qquad \Delta H = -350 \text{ kJ}$$
$$\underline{SnCl_2(s) + Cl_2(g) \rightarrow SnCl_4(l) \qquad \Delta H = -195 \text{ kJ}}$$

Add up both reactions to obtain:

$$Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l) \qquad \Delta H = -545 \text{ kJ}$$

Calculating the Enthalpy Change for the Combustion of Methane

$$C(s, graphite) + 2\,H_2(g) + 2\,O_2(g)$$

1 Decomposition $(+74.6\ kJ)$

2a Formation of $CO_2(g)$ $(-393.5\ kJ)$

$$CH_4(g) + 2\,O_2(g)$$

$$CO_2(g) + 2\,H_2(g) + O_2(g)$$

$$\Delta H_{rxn}° = -802.5\ kJ$$

2b Formation of $2\,H_2O(g)$ $(-483.6\ kJ)$

Enthalpy

$$CO_2(g) + 2\,H_2O(g)$$

Calculating the Enthalpy Change
for the Combustion of Methane

$CH_4(g) + 2O_2(g) \rightarrow C(s) + 2O_2(g) + 2H_2(g)$ $\Delta H = +74.6$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$

$O_2(g) + 2\,H_2(g) \rightarrow 2\,H_2O(g)$ $\Delta H = -483.6$

$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$ $\Delta H = -802.5$

Sample 1 - Calculate the Enthalpy Change in the Reaction from theory

$$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$$

1. Write formation reactions for each compound from its elements and determine the $\Delta H_f°$ for each:

$$2\ C(s,\ gr) + H_2(g) \rightarrow C_2H_2(g) \qquad \Delta H_f° = +227.4\ kJ/mol$$

$$C(s,\ gr) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_f° = -393.5\ kJ/mol$$

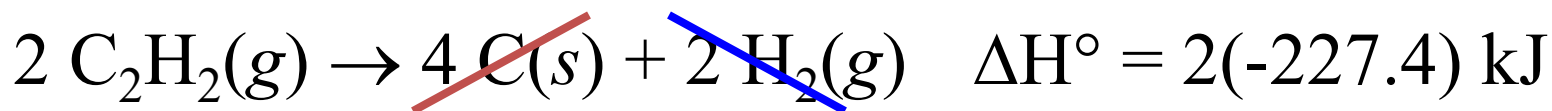$$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H_f° = -285.8\ kJ/mol$$

These values are the ones found in the appendix;
The equations are mutual knowledge so not written

Sample 1 - Calculate the Enthalpy Change in the Reaction from theory

$$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$$

2. Arrange equations so they add up to desired reaction

$2\ C_2H_2(g) \rightarrow 4\ C(s) + 2\ H_2(g) \quad \Delta H° = 2(-227.4)\ kJ$

$4\ C(s) + 4\ O_2(g) \rightarrow 4CO_2(g) \quad \Delta H° = 4(-393.5)\ kJ$

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) \quad \Delta H° = 2(-285.8)\ kJ$

$$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$$
$$\Delta H = -2600.4\ kJ$$
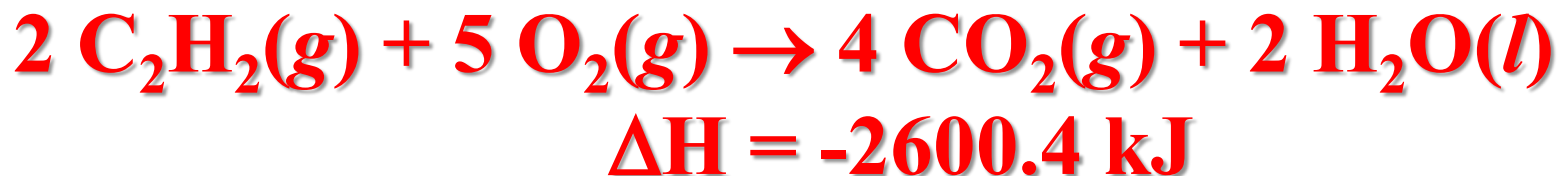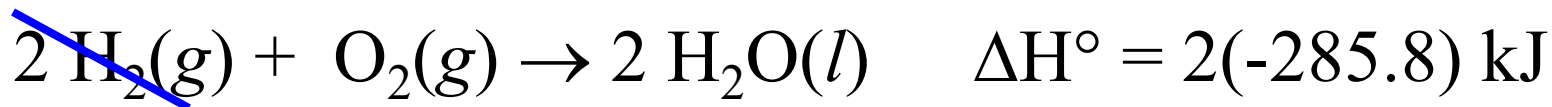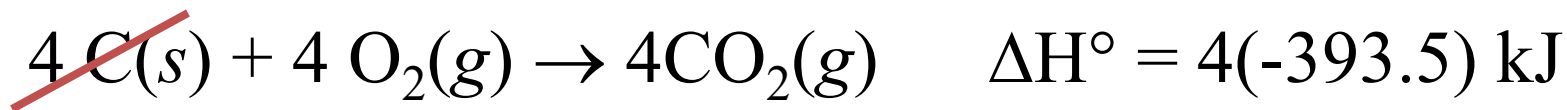
Lecture Questions on Hess's Law

1. $2C(graphite) + O_2(g) \rightarrow 2CO (g)$; $\Delta H = ?$
Consider:

$CO_2(g) \rightarrow CO(g) + \frac{1}{2} O_2 (g)$; $\Delta H = +283.0$ kJ
$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kJ

1) CO is a product so we keep the order but multiply by 2
2) Since that makes 2 CO_2 which must cancel out, we double eqtn 2

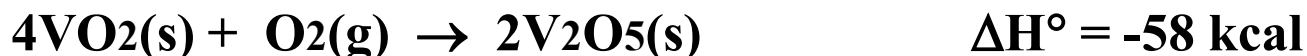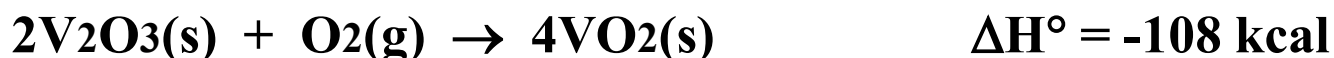$2CO_2(g) \rightarrow 2CO(g) + O_2 (g)$ $\Delta H = 2(+283.0)$ kJ
$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$ $\Delta H = 2(-393.5)$ kJ

$2C(s) + 2O_2(g) \rightarrow 2CO(g) + O_2 (g)$

$\Delta H = -221$ kJ

ACTIVITY on Hess's law
answers

1. Use the standard heats of reaction given below to determine $\Delta H°$ for the following reaction (in kcal): $3V_2O_3(s) \rightarrow V_2O_5(s) + 4VO(s)$.

$$4VO(s) + O_2(g) \rightarrow 2V_2O_3(s) \qquad \Delta H° = -180 \text{ kcal}$$
$$2V_2O_3(s) + O_2(g) \rightarrow 4VO_2(s) \qquad \Delta H° = -108 \text{ kcal}$$
$$4VO_2(s) + O_2(g) \rightarrow 2V_2O_5(s) \qquad \Delta H° = -58 \text{ kcal}$$

$$2V_2O_3(s) \rightarrow 4VO(s) + O_2(g) \qquad \Delta H° = +180 \text{ kcal}$$
$$V_2O_3(s) + \tfrac{1}{2} O_2(g) \rightarrow 2VO_2(s) \qquad \Delta H° = -108/2 \text{ kcal}$$
$$2VO_2(s) + \tfrac{1}{2} O_2(g) \rightarrow V_2O_5(s) \qquad \Delta H° = -58/2 \text{ kcal}$$

$$3V_2O_3(s) \rightarrow V_2O_5(s) + 4VO(s).$$

1st eqtn is reversed; the 2nd & 3rd eqtn's are halved. So
DHt = -(-180) + (-108/2) + (-58/2) = +97 kcal

2. Acetic acid is contained in vinegar. Suppose the following occurred:
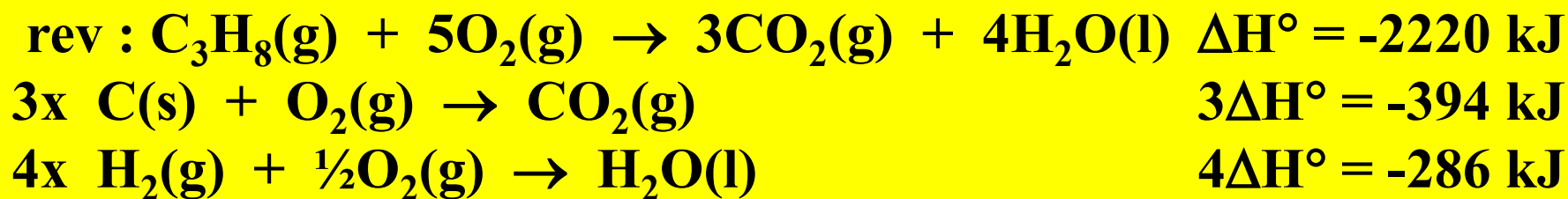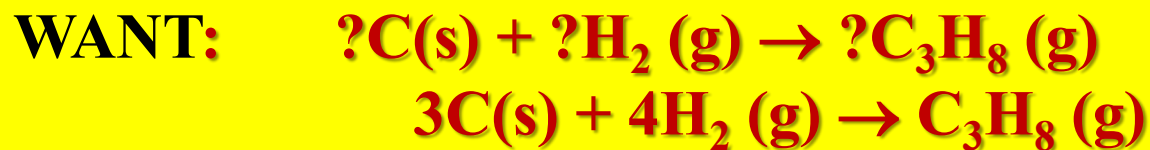
$$2C_{(graphite)} + 2\ H_{2\ (g)} + O_{2(g)} \rightarrow CH_3COOH_{(l)};\ \Delta H=?$$

$$HC_2H_3O_{2(l)} + 2\ O_{2(g)} \rightarrow 2\ CO_{2(g)} + 2\ H_2O_{(l)};\ \Delta H= -871\ kJ$$
$$H_2(g) + \tfrac{1}{2}\ O_2(g) \rightarrow H_2O(l)\ ;\ \Delta H = -286\ kJ$$
$$C_{(graphite)} + O_2(g) \rightarrow CO_2\ (g)\ ;\ \Delta H = -394\ kJ$$

Eqtn 1 must be reversed; eqnt 2 & 3 doubled; so

$$+871 + 2(-286) + 2(-394) = -489\ kJ$$

1. Consider the synthesis of propane from solid carbon and hydrogen gas. Determine the enthalpy change for 1 mol of gaseous propane given the following thermochemical data:

WANT: $?C(s) + ?H_2 (g) \rightarrow ?C_3H_8 (g)$

$3C(s) + 4H_2 (g) \rightarrow C_3H_8 (g)$

rev : $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H° = -2220$ kJ

3x $C(s) + O_2(g) \rightarrow CO_2(g)$ $3\Delta H° = -394$ kJ

4x $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $4\Delta H° = -286$ kJ

$3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g)$ $+2220$ kJ

$3 C(s) + 3 O_2(g) \rightarrow 3CO_2(g)$ $-(3 \times 394$ kJ$)$

$4H_2(g) + 2O_2(g) \rightarrow 4H_2O(l)$ $-(4 \times 286$ kJ$)$

-106 kJ
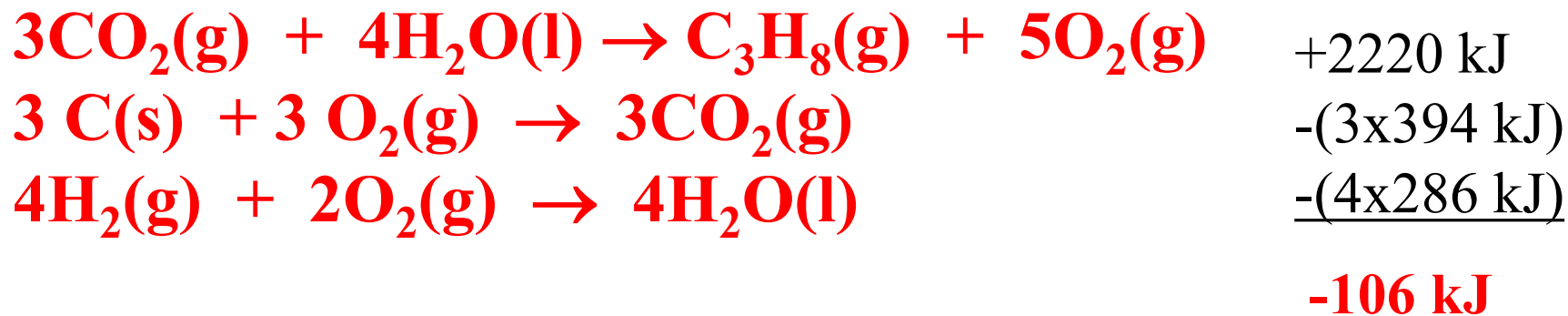
Standard Enthalpies of Formation ($\Delta H_f°$)

the change in enthalpy for the reaction that forms 1 mol of the compound from its elements, with all substances in their standard states (i.e. 298 K).

i. A table of Standard Heats of Formation for some compounds is found in your textbook

ii. ΔH for a reaction is equal to the sum of the heats of formation of the product compounds minus the sum of the heats of formation of the reactant compounds. Using the symbol Σ to represent the "sum of":

$$\Delta H_{rxn}° = \Sigma\, n\Delta H_f°(\text{products}) - \Sigma\, m\Delta H_f°(\text{reactants})$$

where *n* and *m* are the stoichiometric coefficients of the reaction.

Sample 2 - Calculate the Enthalpy Change in the Reaction using the appendix tables

$$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$$

$\Delta H°_{reaction} = \Sigma\ n\ \Delta H_f°(products) - \Sigma\ n\ \Delta H_f°(reactants)$

$$\Delta H_{rxn} = [(4 \cdot \Delta H_{CO2} + 2 \cdot \Delta H_{H2O}) - (2 \cdot \Delta H_{C2H2} + 5 \cdot \Delta H_{O2})]$$

$$\Delta H_{rxn} = [(4 \cdot (-393.5) + 2 \cdot (-285.8)) - (2 \cdot (+227.4) + 5 \cdot (0))]$$

$\Delta H_{rxn} = -2600.4\ kJ$

1. Calculate the standard enthalpy of reaction for the following reaction: $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$
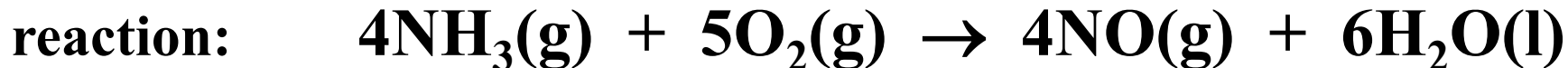
$\Delta H_f°(NH_3) = -132.5 \ kJ/mol; \ \Delta H_f°(NO) = 90.37 \ kJ/mol; \ \Delta H_f°(H_2O) = -285.83 \ kJ/mol$

$\Delta H°_{reaction} = \Sigma \ n \ \Delta H_f°(products) - \Sigma \ n \ \Delta H_f°(reactants)$
$= [4NO + 6 \ H_2O] - [4NH_3 + 5O_2]$
$= [4(90.37) + 6(-285.83)] - [4(-132.5) + 5(0)]$
$= -1353.5 - (-530) = $ **-823.5 kJ**

2. Use the enthalpy of combustion of propane gas to calculate the enthalpy of formation of propane gas.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \ \ \Delta H_c° = $ **-2220 kJ**
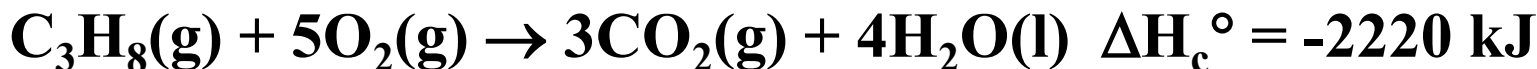
$\Delta H_f°(CO_2) = -393.5 \ kJ/mol; \ \Delta H_f°(H_2O) = -285.83 \ kJ/mol$

$\Delta H°_{reaction} = \Sigma \ n \ \Delta H_f°(products) - \Sigma \ n \ \Delta H_f°(reactants)$
$-2220 = [3CO_2 + 4 \ H_2O] - [C_3H_8 + 5O_2]$
$-2220 = [3(-393.5) + 4(-285.83)] - [(X) + 5(0)]$
$-2220 = -2323.82 - X$

X = -103.82 kJ

Heat of Formation Values

ΔH_f° (kJ/mol) (concentration of aqueous solutions is 1M)

Substance	ΔH_f°	Substance	ΔH_f°	Substance	ΔH_f°	Substance	ΔH_f°
Ag(s)	0	CsCl(s)	−443.0	H_3PO_4(aq)	−1271.7	NaBr(s)	−361.1
AgCl(s)	−127.0	Cs_2SO_4(s)	−1443.0	H_2S(g)	−20.6	NaCl(s)	−411.2
AgCN(s)	146.0	CuI(s)	−67.8	H_2SO_3(aq)	−608.8	$NaHCO_3$(s)	−950.8
Al_2O_3	−1675.7	CuS(s)	−53.1	H_2SO_4(aq)	−814.0	$NaNO_3$(s)	−467.9
$BaCl_2$(aq)	−855.0	Cu_2S(s)	−79.5	$HgCl_2$(s)	−224.3	NaOH(s)	−425.8
$BaSO_4$	−1473.2	$CuSO_4$(s)	−771.4	Hg_2Cl_2(s)	−265.4	Na_2CO_3(s)	−1130.7
BeO(s)	−609.4	F_2(g)	0	Hg_2SO_4(s)	−743.1	Na_2S(s)	−364.8
$BiCl_3$(s)	−379.1	$FeCl_3$(s)	−399.49	I_2(s)	0	Na_2SO_4(s)	−1387.1
Bi_2S_3(s)	−143.1	FeO(s)	−272.0	K(s)	0	NH_4Cl(s)	−314.4
Br_2	0	FeS(s)	−100.0	KBr(s)	−393.8	O_2(g)	0
CCl_4(l)	−128.2	Fe_2O_3(s)	−824.2	$KMnO_4$(s)	−837.2	P_4O_6(s)	−1640.1
CH_4(g)	−74.6	Fe_3O_4(s)	−1118.4	KOH	−424.6	P_4O_{10}(s)	−2984.0
C_2H_2(g)	227.4	H(g)	218.0	LiBr(s)	−351.2	$PbBr_2$(s)	−278.7
C_2H_4(g)	52.4	H_2(g)	0	LiOH(s)	−487.5	$PbCl_2$(s)	−359.4
C_2H_6(g)	−84.0	HBr(g)	−36.3	Mn(s)	0	SF_6(g)	−1220.5
CO(g)	−110.5	HCl(g)	−92.3	$MnCl_2$(aq)	−555.0	SO_2(g)	−296.8
CO_2(g)	−393.5	HCl(aq)	−167.159	$Mn(NO_3)_2$(aq)	−635.5	SO_3(g)	−454.5
CS_2(l)	89.0	HCN(aq)	108.9	MnO_2(s)	−520.0	SrO(s)	−592.0
Ca(s)	0	HCHO	−108.6	MnS(s)	−214.2	TiO_2(s)	−944.0
$CaCO_3$(s)	−1206.9	HCOOH	−425.0	N_2(g)	0	TlI(s)	−123.8
CaO(s)	−634.9	HF(g)	−273.3	NH_3(g)	−45.9	UCl_4(s)	−1019.2
$Ca(OH)_2$(s)	−985.2	HI(g)	26.5	NH_4Br(s)	−270.8	UCl_6(s)	−1092.0
Cl_2(g)	0	H_2O(l)	−285.8	NO(g)	91.3	Zn(s)	0
Co_3O_4(s)	−891.0	H_2O(g)	−241.8	NO_2(g)	33.2	$ZnCl_2$(aq)	−415.1
CoO(s)	−237.9	H_2O_2(l)	−187.8	N_2O(g)	81.6	ZnO(s)	−350.5
Cr_2O_3(s)	−1139.7	H_3PO_2(l)	−595.4	Na(s)	0	$ZnSO_4$(s)	−982.8

Heat of Formation Values

ΔH_f° (kJ/mol) (concentration of aqueous solutions is 1M)

Substance	ΔH_f°	Substance	ΔH_f°	Substance	ΔH_f°	Substance	ΔH_f°
$Ag(s)$	0	$CsCl(s)$	−443.04	$H_3PO_4(aq)$	−1279.0	$NaBr(s)$	−361.062
$AgCl(s)$	−127.068	$Cs_2SO_4(s)$	−1443.02	$H_2S(g)$	−20.63	$NaCl(s)$	−411.153
$AgCN(s)$	146.0	$CuI(s)$	−67.8	$H_2SO_3(aq)$	−608.81	$NaHCO_3(s)$	−950.8
Al_2O_3	−1675.7	$CuS(s)$	−53.1	$H_2SO_4(aq)$	−814.0	$NaNO_3(aq)$	−447.48
$BaCl_2(aq)$	−871.95	$Cu_2S(s)$	−79.5	$HgCl_2(s)$	−224.3	$NaOH(s)$	−425.609
$BaSO_4$	−1473.2	$CuSO_4(s)$	−771.36	$Hg_2Cl_2(s)$	−265.22	$Na_2CO_3(s)$	−1130.7
$BeO(s)$	−609.6	$F_2(g)$	0	$Hg_2SO_4(s)$	−743.12	$Na_2S(aq)$	−447.3
$BiCl_3(s)$	−379.1	$FeCl_3(s)$	−399.49	$I_2(s)$	0	$Na_2SO_4(s)$	−1387.08
$Bi_2S_3(s)$	−143.1	$FeO(s)$	−272.0	$K(s)$	0	$NH_4Cl(s)$	−314.4
Br_2	0	$FeS(s)$	−100.0	$KBr(s)$	−393.798	$O_2(g)$	0
$CCl_4(l)$	−128.2	$Fe_2O_3(s)$	−824.2	$KMnO_4(s)$	−837.2	$P_4O_6(s)$	−1640.1
$CH_4(g)$	−74.81	$Fe_3O_4(s)$	−1118.4	KOH	−424.764	$P_4O_{10}(s)$	−2984.0
$C_2H_2(g)$	226.73	$H(g)$	217.965	$LiBr(s)$	−351.213	$PbBr_2(s)$	−278.7
$C_2H_4(g)$	52.26	$H_2(g)$	0	$LiOH(s)$	−484.93	$PbCl_2(s)$	−359.41
$C_2H_6(g)$	−84.68	$HBr(g)$	−36.40	$Mn(s)$	0	$SF_6(g)$	−1220.5
$CO(g)$	−110.525	$HCl(g)$	−92.307	$MnCl_2(aq)$	−555.05	$SO_2(g)$	−296.830
$CO_2(g)$	−393.509	$HCl(aq)$	−167.159	$Mn(NO_3)_2(aq)$	−635.5	$SO_3(g)$	−454.51
$CS_2(l)$	89.70	$HCN(aq)$	108.9	$MnO_2(s)$	−520.03	$SrO(s)$	−592.0
$Ca(s)$	0	$HCHO$	−108.57	$MnS(s)$	−214.2	$TiO_3(s)$	−939.7
$CaCO_3(s)$	−1206.9	$HCOOH(l)$	−424.72	$N_2(g)$	0	$TlI(s)$	−123.5
$CaO(s)$	−635.1	$HF(g)$	−271.1	$NH_3(g)$	−46.11	$UCl_4(s)$	−1019.2
$Ca(OH)_2(s)$	−986.09	$HI(g)$	26.48	$NH_4Br(s)$	−270.83	$UCl_5(s)$	−1059
$Cl_2(g)$	0	$H_2O(l)$	−285.830	$NO(g)$	90.25	$Zn(s)$	0
$Co_3O_4(s)$	−891	$H_2O(g)$	−241.818	$NO_2(g)$	33.18	$ZnCl_2(aq)$	−488.19
$CoO(s)$	−237.94	$H_2O_2(l)$	−187.8	$N_2O(g)$	82.05	$ZnO(s)$	−348.28
$Cr_2O_3(s)$	−1139.7	$H_3PO_4(l)$	−595.4	$Na(s)$	0	$ZnSO_4(aq)$	−1063.15

SELF-STUDY QUIZ on Standard Enthalpy:

1. **Calculate the standard enthalpy of reaction for the following reactions:**
    a) $2 NO(g) + O_2(g) \rightarrow 2NO_2(g)$
    b) $2 NH_3(g) + \frac{7}{2} O_2(g) \rightarrow 2 NO_2(g) + 3 H_2O(g)$
    c) $Fe_2O_3(s) + 3CO(g) \rightarrow 2 Fe(s) + 3 CO_2(g)$
    d) $2BaSO_4(s) \rightarrow 2BaO(s) + 2SO_2(g) + O_2 (g)$
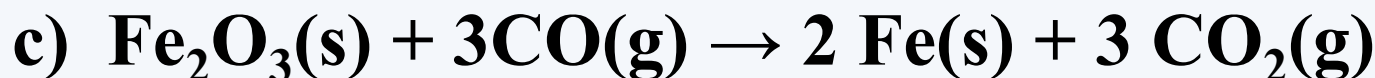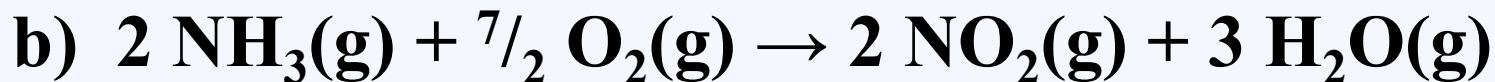
2. (a) Calculate the heat required to combust 10.0 g of nitrogen monoxide.
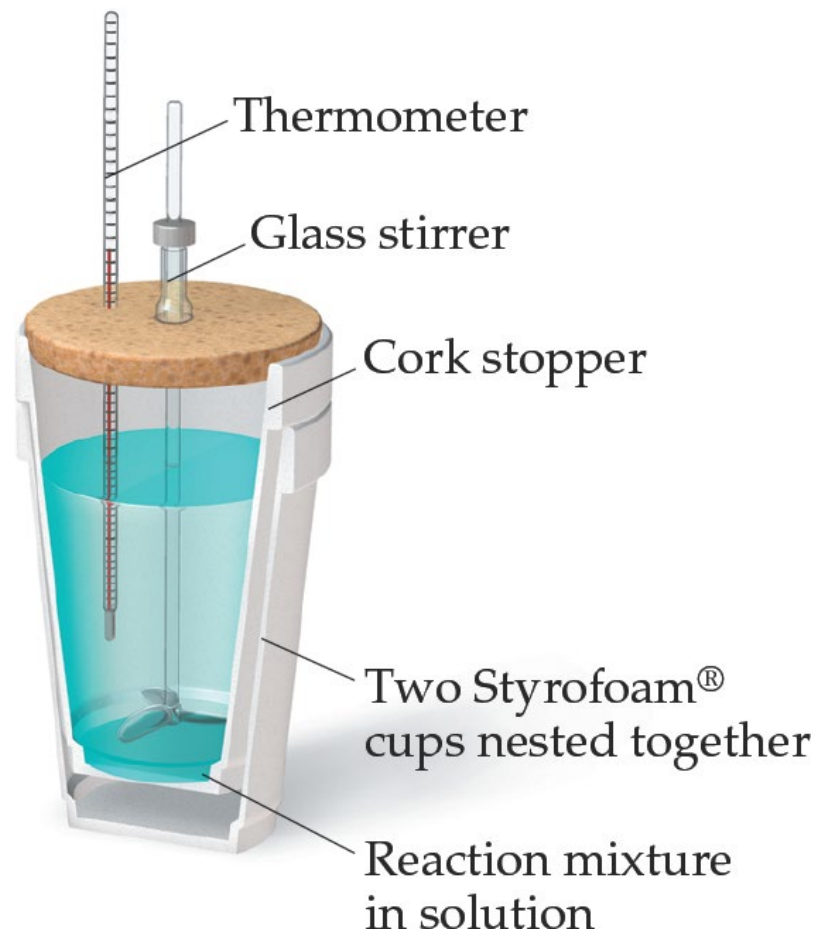
(b) Calculate the heat required to combust 25.0 g of ammonia.

(c) Calculate the heat required to produce 25.0 g of iron from iron(III) oxide.

(d) Calculate the heat required to decompose 10.0 g of barium sulfate. ΔH_f^o (BaO) = -553.5 kJ/mol

Calorimetry

- Since we cannot know the exact enthalpy of the reactants and products, we measure ΔH through **calorimetry**, the measurement of heat flow.

- The instrument used to measure heat flow is called a **calorimeter**.

CANVAS LECTURE ACTIVITY!!!

Thermometer

Glass stirrer

Cork stopper

Two Styrofoam® cups nested together

Reaction mixture in solution

Heat Capacity and Specific Heat

The amount of energy required to raise the temperature of a substance by 1 K (1 degree Celsius) is its **heat capacity**. If the amount of the substance heated is one gram, it is the **specific heat**. If the amount is one mole, it is the **molar heat capacity**.

Table 5.2 Specific Heats of Some Substances at 298 K

Elements		Compounds	
Substance	**Specific Heat (J/g-K)**	**Substance**	**Specific Heat (J/g-K)**
$N_2(g)$	1.04	$H_2O(l)$	4.18
$Al(g)$	0.90	$CH_4(g)$	2.20
$Fe(s)$	0.45	$CO_2(g)$	0.84
$Hg(l)$	0.14	$CaCO_3(s)$	0.82

1.000 g $H_2O(l)$
$T_{final} = 15.5\,°C$

+ 4.184 J (1 cal) of heat

1.000 g $H_2O(l)$
$T_{initial} = 14.5\,°C$

Calorimetry – measurement of heat flow

HEAT CAPACITY: The quantity of heat needed to raise the temperature of a substance one degree Celsius (or one Kelvin). **If the system is a mole of a substance, we use the term *molar heat capacity***

$$q = C_p \, \Delta T$$

SPECIFIC HEAT: The quantity of heat required to raise the temperature of one gram of a substance by one degree Celsius (or one Kelvin).

$$q = s \times m \times \Delta T$$

***NOTE: BOTH s and C will be provided on a case-by-case basis. You MUST memorize the specific heat of water, 1 cal/g °C = 4.184 J/g °C. Both C_p & s are chemical specific constants found in the textbook or CRC Handbook.

LAW OF CONSERVATION OF ENERGY (LCE)

- **The law of conservation of energy (the first law of thermodynamics), when related to heat transfer between two objects, can be stated as:**

The heat lost by the hot object = the heat gained by the cold object

$$-q_{hot} = q_{cold}$$

$$-m_h \times s_h \times \Delta T_h = m_c \times s_c \times \Delta T_c$$

where $\Delta T = T_{final} - T_{initial}$

Lecture Questions on SPECIFIC HEAT & LCE

1. **Exactly 500.00 kJ of heat is absorbed by a sample of gaseous He. The temperature increases by 15.0 K.**

   a) Calculate the heat capacity of the sample.

   b) the sample weighs 6.42 kg. Compute the specific heat and molar heat capacity of He.

A) $q = C_p \, \Delta T$

$500.0 \times 10^3 \, J = C_p \, (15 \, K)$

$C_p = 33.3 \, kJ/K$

B) $q = s \times m \times \Delta T$

$500 \times 10^3 J = 6.42 \times 10^3 \, g \, (s) \, 15$

$s = 5.18 \, J/g^oC$

B)

Molar heat capacity $= C_p / n$

$(33.3 \, kJ/K) / n$

So we need moles:

$6.42 \times 10^3 \, g \, (1 \, mol/4 \, g) = 1605 \, mol$

So:

$33.3 \times 10^3 / 1605 = \textbf{20.7 kJ/mol K}$

2. Assuming no heat is lost, what mass of cold water at 0.00ºC is needed to cool 100.0 g of water at 97.6ºC to 12.0 ºC?

$$-m_h \times s_h \times \Delta T_h = m_c \times s_c \times \Delta T_c$$

$$-q_{hot} = q_{cold}$$

$$-m_h \times s_h \times \Delta T_h = m_c \times s_c \times \Delta T_c$$

$$-(100g)(1 \text{ cal/g}^o\text{C})(12-97.6) = m (1 \text{ cal/g}^o\text{C}) (12-0)$$

$$8560 = 12m$$

$$\textbf{m = 713 g}$$

3. Calculate the specific heat of an unknown metal if a 92.00 g piece at 100.0ºC is dropped into 175.0 mL of water at 17.8 ºC. The final temperature of the mixture was 39.4ºC.

$$-q_{hot} = q_{cold}$$

$$-m_h \times s_h \times \Delta T_h = m_c \times s_c \times \Delta T_c$$

175 mL (1g/1mL) = 175 g density of water

$$-(92g)(s)(39.4 - 100) = 175g\ (4.184\ J/g^oC)\ (39.4 - 17.8)$$

$$5575.2s = 3780$$

s = 0.678 cal/gºC

NOTE: These examples are all physical changes

ACTIVITY on Specific heat & LCE

1. Determine the energy (in kJ) required to raise the temperature of 100.0 g of water from 20.0 ºC to 85.0 ºC?

2. Determine the specific heat of an unknown metal that required 2.56 kcal of heat to raise the temperature of 150.00 g from 15.0 ºC to 200.0 ºC?

3. Assuming no heat is lost to the surrounding, what will be the final temperature when 50.0 g of water at 10.0 ºC is mixed with 10.0 g of water at 50.0 ºC?

Exchanging Energy Between System and Surroundings
(chemical changes)

- exchange of heat energy

  q = mass x specific heat x ΔTemperature

- exchange of work

  $w = -$Pressure x ΔVolume
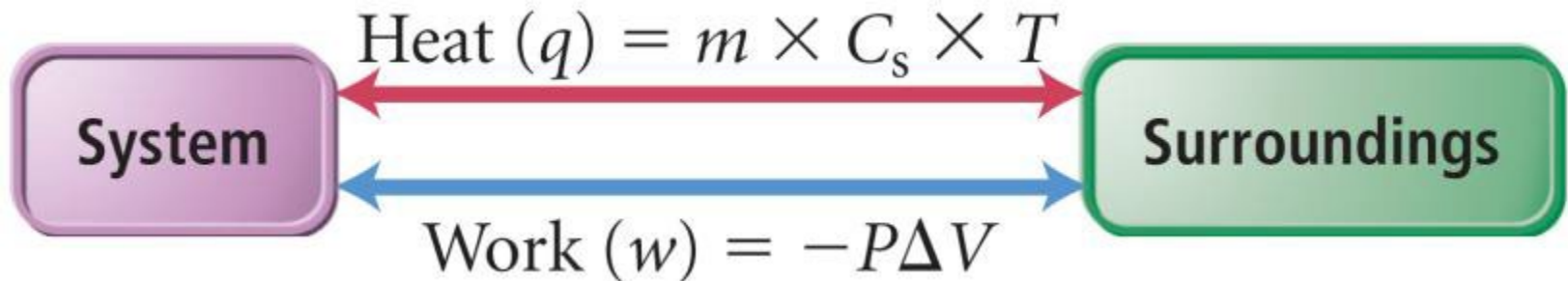
Bomb Calorimeter

- used to measure ΔE because it is a constant volume system

System (reaction) ←— Heat —→ **Surroundings**

Observe change in temperature

The Bomb Calorimeter

Thermometer

Ignition wire

Stirrer

Water

Tightly sealed "bomb"

Sample

Oxygen
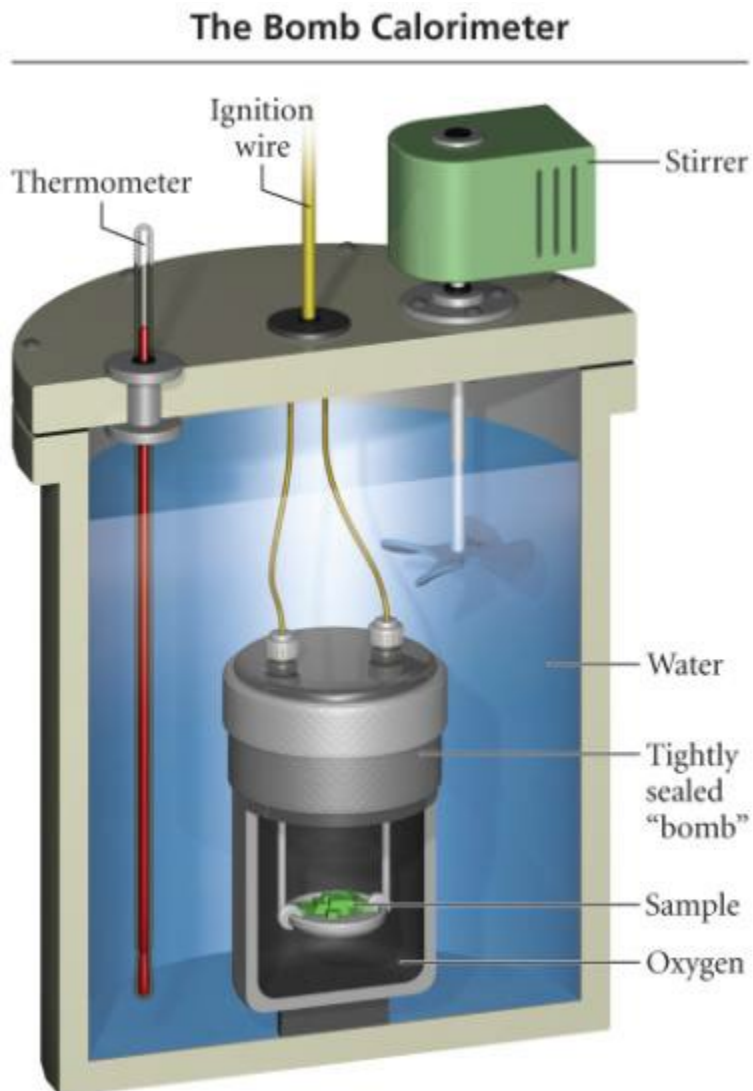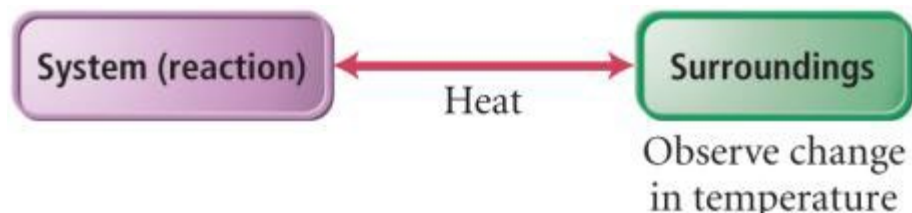
Bomb Calorimetry

- Reactions can be carried out in a sealed "bomb" such as this one.

- The heat absorbed (or released) by the water is a very good approximation of the enthalpy change for the reaction.

- $q_{rxn} = -C_{cal} \times \Delta T$

Stirrer

Sample ignition wires

$+$ $-$

Thermometer

Insulated container

Bomb (reaction chamber)

Water
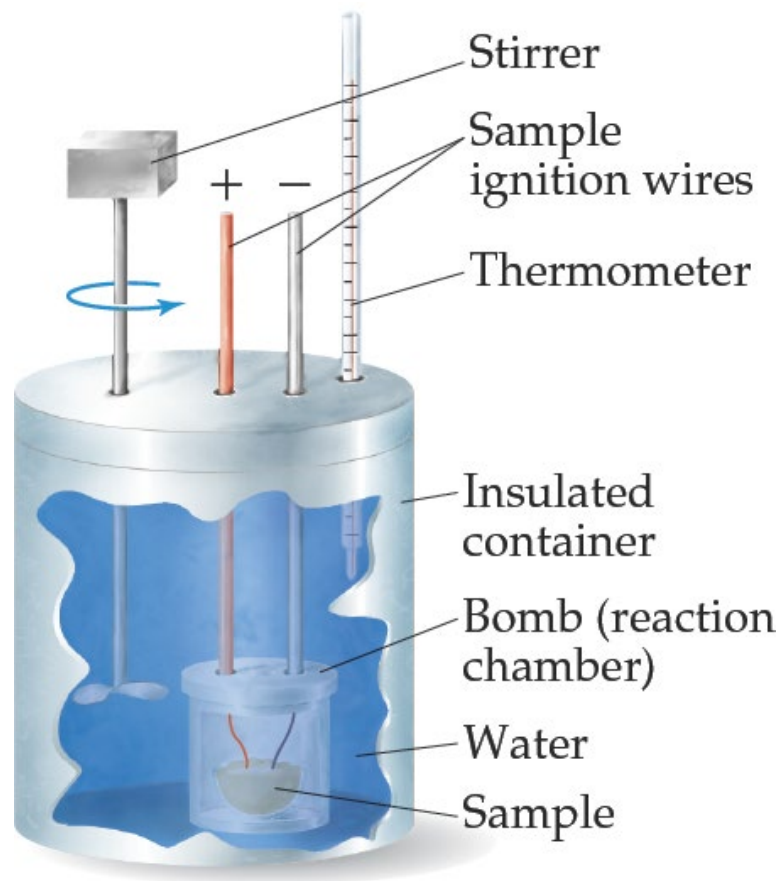
Sample

Bomb Calorimetry

- Because the volume in the bomb calorimeter is constant, what is measured is really the change in internal energy, ΔE, not ΔH.

- For most reactions, the difference is very small.

Stirrer

Sample ignition wires

Thermometer

Insulated container

Bomb (reaction chamber)

Water
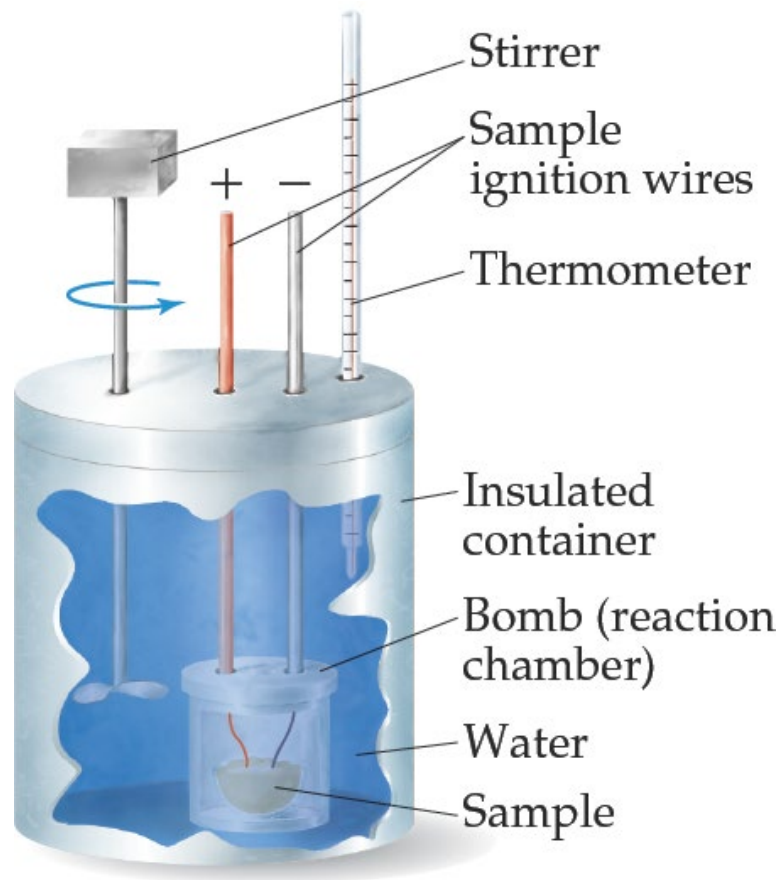
Sample

Example – When 1.010 g of sugar is burned in a bomb calorimeter, the temperature rises from 24.92°C to 28.33°C. If C_{cal} = 4.90 kJ/°C, find ΔE for burning 1 mole

Given:	1.010 g $C_{12}H_{22}O_{11}$, T_1 = 24.92°C, T_2 = 28.33°C, C_{cal} = 4.90 kJ/°C
Find:	ΔE_{rxn}, kJ/mol
Concept Plan:	$\boxed{C_{cal}, \Delta T} \Rightarrow \boxed{q_{cal}}$ $\qquad$ $\boxed{q_{cal}} \Rightarrow \boxed{q_{rxn}}$ $q_{cal} = C_{cal} \times \Delta T$ $\qquad\qquad$ $q_{rxn} = - q_{cal}$
Relationships:	$q_{cal} = C_{cal} \times \Delta T = -q_{rxn}$ $\qquad$ $\Delta E = \dfrac{q_{rxn}}{\text{mol } C_{12}H_{22}O_{11}}$ MM $C_{12}H_{22}O_{11}$ = 342.3 g/mol
Solution:	$q_{cal} = C_{cal} \times \Delta T$ $\qquad$ $1.010\ g\ C_{12}H_{22}O_{11} \times \dfrac{1\ mol\ C_{12}H_{22}O_{11}}{342.3\ g}$ $\qquad$ $\Delta E = \dfrac{q_{rxn}}{\text{mol } C_{12}H_{22}O_{11}} = \dfrac{-16.7\ kJ}{2.5906 \times 10^{-3}\ mol}$ $= 4.90 \frac{kJ}{°C} \times 3.41\ °C = 16.7\ kJ$ $\qquad$ $= 2.5906 \times 10^{-3}\ mol$ $\Delta T = 28.33\ °C - 24.92\ °C$ $\Delta T = 3.41\ °C$ $\qquad$ $q_{rxn} = -q_{cal} = -16.7\ kJ$ $\qquad$ $= -5.66 \times 10^3\ kJ/mol$
Check:	the units and sign are correct

Calorimetry and Chemical Reactions

A heat of reaction, q_{rxn}, is the quantity of heat exchanged between a system and its surroundings when a chemical reaction occurs within the system at constant temperature. If this reaction occurs in an isolated system, the reaction produces a change in the thermal energy of the system. That is, the overall temperature either increases **(exothermic; becomes warmer)** or decreases **(endothermic; becomes cooler)**.
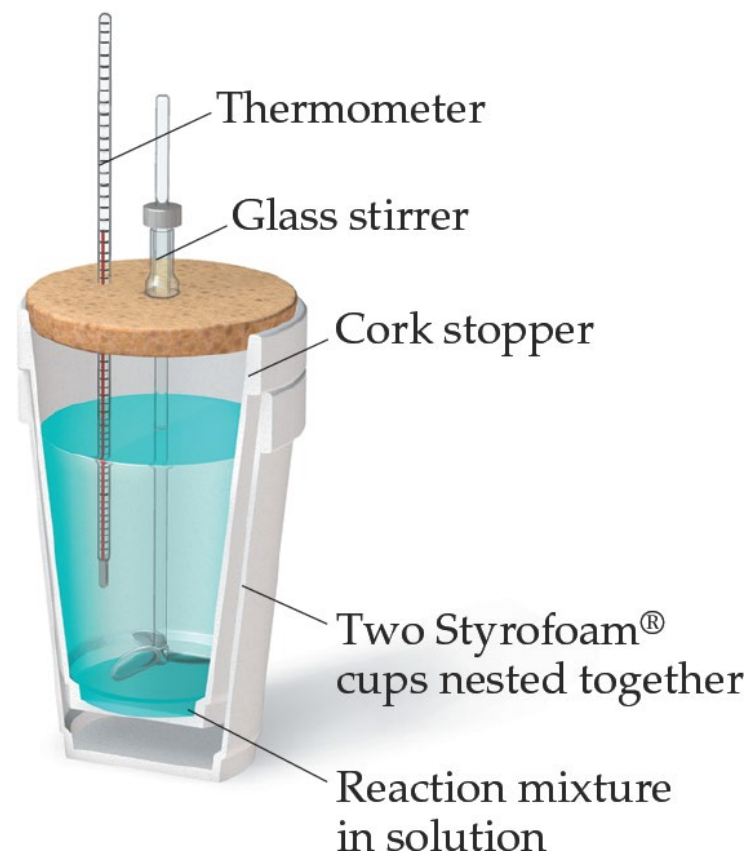
Heats of reaction are experimentally determined in a calorimeter, a device for measuring quantities of heat. Two common calorimeters are: **(1) bomb calorimeter (used for combustion reactions)** and **(2) "coffee-cup" calorimeter (a simple calorimeter for general chemistry laboratory purposes built from styrofoam cups).** As previously mentioned, the heat of reaction is the quantity of heat that the system would have to *lose* to its surroundings to be restored to its initial temperature. This quantity of heat is the *negative* of the thermal energy gained by the calorimeter and its contents ($q_{calorimeter}$).

Therefore: $q_{rxn} = -q_{calorimeter}$.

Constant Pressure Calorimetry

- By carrying out a reaction in aqueous solution in a simple calorimeter, the heat change for the system can be found by measuring the heat change for the water in the calorimeter.

- The specific heat for water is 4.184 J/g·K. We use this value for dilute solutions.

- We can calculate ΔH for the reaction with this equation:

$$q_{soln} = C_s \times m_{soln} \times \Delta T = -q_{rxn}$$

Thermometer

Glass stirrer

Cork stopper

Two Styrofoam® cups nested together

Reaction mixture in solution

Example :   **Measuring ΔH Using a Coffee-Cup Calorimeter**

When a student mixes 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 to 27.5 °C. Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming that the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100 mL, that its density is 1.0 g/mL, and that its specific heat is 4.18 J/g-K.

Solution:

Analyze: Mixing solutions of HCl and NaOH results in an acid-base reaction:

$$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$$

We need to calculate the heat produced per mole of HCl, given the temperature increase of the solution, the number of moles of HCl and NaOH involved, and the density and specific heat of the solution.

Plan The total heat produced can be calculated using q=msΔT. The number of moles of HCl consumed in the reaction must be calculated from the volume and molarity of this substance, and this amount is then used to determine the heat produced per mol HCl.

Solution

1) Because the total volume of the solution is 100 mL, its mass is:
   (100 mL)(1.0 g/mL) = 100 g

2) The temperature change is: $\Delta T = 27.5\ °C - 21.0\ °C = 6.5\ °C = 6.5\ K$

3) Solving for the product side:

$$q_{rxn} = -C_s \times m \times \Delta T$$

$$= -(4.18\ J/g\text{-}K)(100\ g)(6.5\ K) = -2.7 \times 10^3\ J = -2.7\ kJ$$

4) Because the process occurs at constant pressure, $\Delta H = q_P = -2.7\ kJ$

To express the enthalpy change on a molar basis, we use the fact that the number of moles of HCl is given by n=MV; where the volume is (50 mL = 0.050 L) and the concentration is (1.0 M = 1.0 mol/L) of the HCl solution:

$$(0.050\ L)(1.0\ mol/L) = 0.050\ mol$$

Thus, the enthalpy change per mole of HCl is:

$$\Delta H = -2.7\ kJ/0.050\ mol = -54\ kJ/mol$$

**Check** ΔH is negative (exothermic), as evidenced by the observed increase in the temperature. The magnitude of the molar enthalpy change seems reasonable.

Calorimetry & Chemical Reactions

1. When a student mixes 50 mL of 1.0 M HNO_3 and 50 mL of 1.0 M $Ca(OH)_2$ in a coffee-cup calorimeter, the temperature of the resultant solution increases from 19.8 °C to 27.5 °C. Calculate the enthalpy change for the reaction (in kJ/mol), assuming that the calorimeter loses only a negligible quantity of heat and the density of the solution is 1.0 g/mL.

Calorimetry & Chemical Reactions

1. **When a student mixes 50 mL of 1.0 M HNO_3 and 50 mL of 1.0 M $Ca(OH)_2$ in a coffee-cup calorimeter, the temperature of the resultant solution increases from 19.8 °C to 27.5 °C. Calculate the enthalpy change for the reaction (in kJ/mol), assuming that the calorimeter loses only a negligible quantity of heat and the density of the solution is 1.0 g/mL.**

$$2HNO_3 + Ca(OH)_2 \rightarrow 2\ H_2O + Ca(NO_3)_2$$
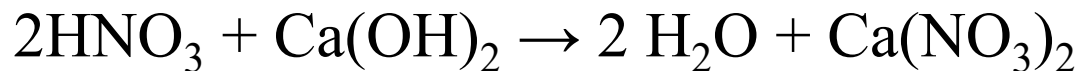
50 mL	50 mL
1.0 M	1.0 M
0.05 mol	0.05 mol

50 + 50 = 100 mL

To calculate molar value we need the limiting reactant:
Nitric acid produces 0.05 moles of water whereas calcium hydroxide produces 0.1 mol of water so n=0.05

Product side: $q = ms\Delta T$

$q = 100g\ (4.184J/g°C)\ (27.5 - 19.8)$

$q = 3221.7J$ or 3.22 kJ   BUT!!!

$q_{products} = -\ q_{reactants}$ so   -3.22kJ

$\Delta H = -q/n$

$\Delta H = -3.22kJ/0.05$ mol

$\Delta H = -64.4$ kJ/mol

Calorimetry & Chemical Reactions

2. A sample of benzene (C_6H_6) weighing 3.51 g was burned in an excess of oxygen in a bomb calorimeter. The temperature of the calorimeter rose from 25.00 °C to 37.18 °C. If the heat capacity was 12.05 kJ/°C, what is the heat of reaction at 25.00°C and 1.00 atm?

This is a bomb calorimetry so $q = C_{cal}\Delta T$

C_6H_6 + 15 O_2 → 6 CO_2 + 3H_2O

3.51g / (78g/mol) = 0.045 mol

$q_{cal} = C_{cal} \times \Delta T = -q_{rxn}$

q = (12.05 kJ/°C) (37.18-25)

q = 146.8 kJ

q_{rxn} = -146.8 kJ

$\Delta E = q_{rxn} / n$

$\Delta E = -146.8kJ / 0.045$ mol

$\Delta E = -3262$ kJ/mol

GROUP 1

When 0.243 g of Mg metal is combined with enough HCl to make 100 mL of solution in a constant-pressure calorimeter, the following reaction occurs: **Mg(s) + 2 HCl(aq)   →   MgCl$_2$(aq) + H$_2$(g)**
If the temperature of the solution increases from 23.0 to 34.1 °C as a result of this reaction, calculate ΔH in kJ/mol Mg. Assume that the solution has a specific heat of 4.18 J/g-°C and a density of 1.00 g/mL.

(a) –19.1 kJ/mol (b) –111 kJ/mol (c) –191 kJ/mol (d) –464 kJ/mol (e) –961 kJ/mol

GROUP 2

When 50.0 mL of 0.100 M AgNO$_3$ and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30 to 23.11 °C. The temperature increase is caused by the following reaction: **AgNO$_3$(aq) + HCl(aq)   →   AgCl(s) + HNO$_3$(aq)**
Calculate ΔH for this reaction in kJ/mol AgNO$_3$, assuming that the combined solution has a mass of 100.0 g & specific heat of 4.18 J/g-°C.

Thermodynamics related to a change in State of Matter.

CHANGES OF STATE

A solid changes to a liquid at its melting point, and a liquid changes to a gas at its boiling point. This warming process can be represented by a graph called a heating curve. This figure shows ice being heated at a constant rate.

When heating ice at a constant rate, energy flows into the ice, the vibration within the crystal increase and the temperature rises (A→B). Eventually, the molecules begin to break free from the crystal and melting occurs (B→C). During the melting process all energy goes into breaking down the crystal structure; the temperature remains constant.
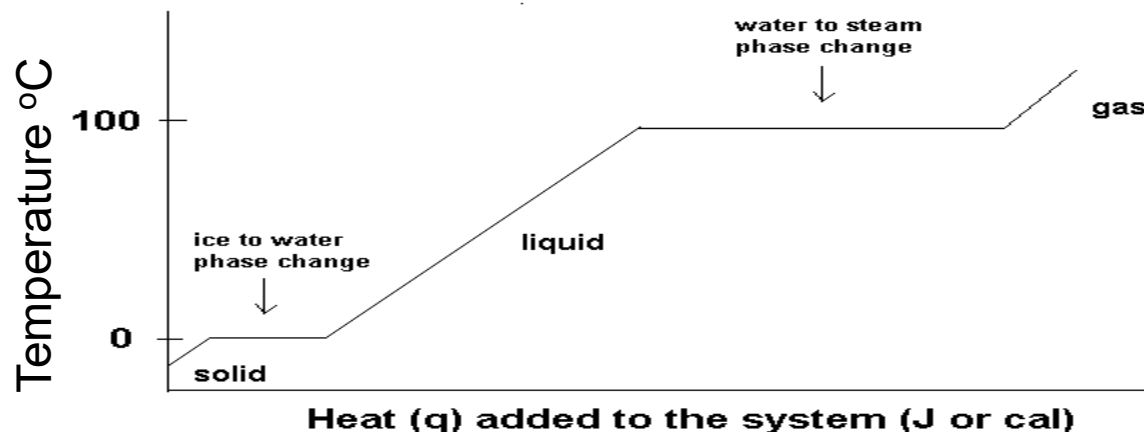
HEATING CURVE
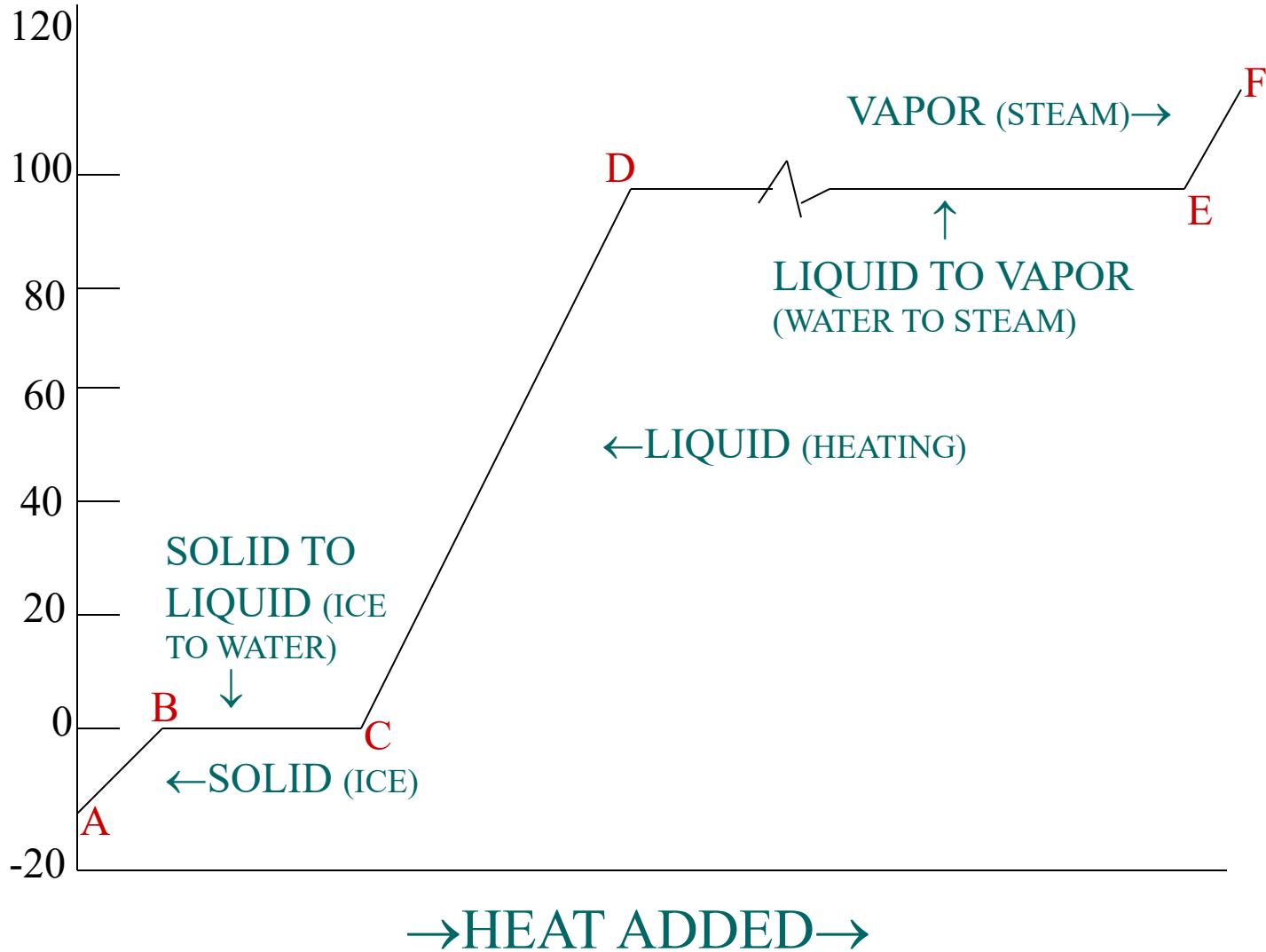
Water and the Changes of State

The energy required to heat (or cool) a solid (or heat/cool a liquid or a gas) can be calculated using $q = ms\Delta T$. It requires additional energy to change states. The energy required to convert a specific amount of the solid to a liquid is known as the heat of fusion ($q = \Delta H_{fus}$) and the energy required to convert a specific amount of a liquid to a gas is the heat of vaporization ($q = \Delta H_{vap}$).

The total amount of energy can be calculated from $q_T = q_1 + q_2 + q_3 \ldots$

Heating curve for water

1) **When ice at 0°C melts to a liquid at 0°C, it absorbs 0.334 kJ of heat/gram. Suppose the heat needed to melt 35.0 g of ice is absorbed from the water contained in the glass. If this water has a mass of 0.210 kg at 21°C, what is the final temperature of the water?**

Practice Problems on phase transition enthalpy

1) When ice at 0°C melts to a liquid at 0°C, it absorbs 0.334 kJ of heat/gram. Suppose the heat needed to melt 35.0 g of ice is absorbed from the water contained in the glass. If this water has a mass of 0.210 kg at 21°C, what is the final temperature of the water?

2) Ethanol, C_2H_5OH, melts at -114°C and boils at 78.0 °C. The heat of fusion is 5.02 kJ/mol and the heat of vaporization is 38.56 kJ/mol. The specific heat of the solid and liquid ethanol are 0.97 J/gK and 2.3 J/gK, respectively. How much heat is required to convert 50.0 g of ethanol at -150.0 °C to the vapor state at 78.0°C?