Thermochemistry

Forms of Energy and Their Conversion

Discussion: Everyday physical objects, such as a golf ball flying through the air), posses two basic forms of energy – what are they?

1.

2.

'Stunt Fish' Demo and Analogy to a Chemical Systems

When energy is transferred or converted to another form, it must eventually appear as *work* and/or *heat* (think about your car)

Recall: The potential energy (enthalpy, H) possessed by elements and compounds is 'stored' within their chemical bonds.

Breaking a chemical bond requires energy (heat)
&
Making a chemical bond releases energy (heat)

Each type of chemical bond has it's own enthalpy (stored chemical potential energy, e.g. O-O = 138 kJ/mole). See Appendix and the '*More Chemical Bonding*' note packet for details

Mathematical Version – The First Law of Thermodynamics (see Appendix)

$$\Delta E = q + w$$

Where: ΔE = change in energy for the system ('dropping the fish')

q = heat energy transferred

w = work performed (PV work for chemical systems, like for the combustion of gasoline in a car engine)

For chemical systems, there is most often no gas evolved, so there is no 'PV' work. Thus…..

$$\Delta E = \boxed{-\Delta H = +q_p} \text{ (first law of thermodynamics)}$$

Where: ΔH = change in 'chemical potential energy' (enthalpy) for the system

q_p = heat energy transferred to or from the chemical system (at constant pressure – i.e. no PV work)

Note: sign convention – heat energy is given out ($+q$) when the internal chemical energy (enthalpy) of the chemical system is reduced ($-\Delta H$). This is what we know as an exothermic process – more on this later.

Exothermic and Endothermic Chemical Processes

Definitions: Before we go any further, it is important to know a few key definitions. Hint: think about the construction of the words themselves to determine their meaning.

Thermochemistry: *Study of the quantity of **heat** absorbed or evolved during a **chemical reaction***

Thermodynamics: *Study of the relationship between **heat** and the other forms of energy involved in a chemical (or physical) process*

Heat*: The energy that flows into or out of a system because of a difference in temperature between the **thermodynamic system** and its **surroundings**.* See slide.

Thermodynamic system (system): *The substance or mixture of substances under study in which (chemical) change occurs*

Surroundings: *Everything in the vicinity of the thermodynamic system. Heat is either lost or gained to or from the surroundings.* See slide.

Enthalpies of Reaction

Recall: All chemical reactions either release (exothermic) or absorb (endothermic) heat energy when going from reactants → products. As we saw in earlier material, this information can be represented quantitatively with a *thermochemical equation*.

Example: CH_4 (g) + $2 O_2$ (g) → CO_2 (g) + $2 H_2O$ (g) ; ΔH = -890.3 kJ

One mole of CH_4 (g) reacts with 2 moles of O_2 (g) to produce chemical products and 890.3 kJ of heat.

Questions: How much heat would be evolved if:

1. 2 moles of CH_4 (g) were combusted in XS oxygen gas?

2. 4 moles of CH_4 (g) were combusted in XS oxygen gas?

Enthalpy is an *extensive* property – it depends on the amount of material involved. *"Two logs thrown on the fire produces twice as much heat as one log"*

Change in Enthalpy, ΔH

Discussion: What does ΔH really mean, in terms of what's going on with the reactants and products in a chemical reaction?

The change in enthalpy (ΔH) is simply a measure of how much 'chemical potential energy' has been either lost or gained by converting the bonds present in the reactants ($H_{reactants}$) into the bonds present in the products ($H_{products}$). Recall that this difference in energy is either lost or gained from the system as heat.

Mathematically

$$\Delta H \ = \ (H_{products} \ - \ H_{reactants})$$

Recall also that:

$$- \Delta H \ = \ +q$$

Since q can be measured experimentally (recall your lab), details pertaining to the enthalpy of the reactants and products involved in a chemical reaction can be determined. This theory underpins all calorimetric investigations

Calorimetry

The amount of heat energy transferred to or from any material or object (thermodynamic system) can be found if its HEAT CAPACITY (C_p), MASS (g) and observed TEMPERATURE CHANGE, ΔT (^{o}C or K), it undergoes are known:

$$q = \ C_p \ x \ m \ x \ \Delta T$$

Where: q = heat energy transferred to or from the system

C_p = specific heat capacity of the system – a constant with units of J/g^{o}C

m = mass of system in grams

ΔT = change in temperature (in K or ^{o}C) of the system.
Defined at T_{final} - $T_{initial}$

Table of Selected Specific Heat Capacities (see Appendix)

Substance	Sp. Ht. Cap. (J/g°C)	Substance	Sp. Ht. Cap. (J/g°C)
Water (l)	4.18	Mercury (l)	0.14
Water (s)	2.03	Carbon (s)	0.71
Aluminum	0.89	Silver (s)	0.24
Iron (s)	0.45	Gold (s)	0.13

Since each material has its own specific heat capacity, similar math applies:

Group work

1. How much heat energy is needed to raise the temperature of 25 g water by 15°C?

2. How much heat energy is needed to raise the temperature of 25 g solid iron by 15°C?

3. How much heat energy would be needed to boil a 330 mL glass of water that is initially at room temperature (25 $^{\circ}$C)? Density H_2O (l) = 1.00 g/mL

4. A blacksmith tosses a 'red hot' iron horseshoe weighing 0.569 kg into a 5.0L bucket of water. If the water in the bucket rises in temperature from 10°C to 20°C, what was the original temperature of the horseshoe? Assume heat is only exchanged between the horseshoe and the water and no heat is lost to the surroundings.

Application to Chemical Systems

Recall: In your recent lab, the change in enthalpy (-ΔH) for the reaction between magnesium and HCl = heat energy (+q) gained by the surrounding solution in the insulated cup.

i.e. $$- \Delta H_{(reaction)} = +q_{(solution)}$$

Remember: q is measured in _____ , the S.I. unit of energy, even though thermodynamic values are typically quoted in _____

Since the solutions used in calorimetry experiments typically contain a relatively low concentration of products:

$$C_{p\ (solution)} \approx C_{p\ (water)} = 4.18\ J/g^oC$$

Worked Example: 33 mL of 1.2 M HCl (aq) is added to 42 mL of a solution containing an excess of NaOH (aq). If a temperature change of $25^oC \to 31.8$ ^oC is observed, calculate ΔH for the reaction. Quote your answer in kJ/mole.

Measuring Heats of Reaction (ΔH)

Calorimetry (measuring heats of reaction, recall your lab) can simply be considered as the practical application of the 1st Law, such as shown immediately above, i.e.:

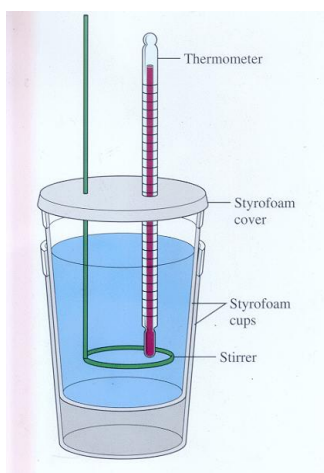$$-\Delta H_{(reaction)} \; = \; +q_{(solution)}$$

Where:

$$q_{(solution)} = \; C_p \; x \; m \; x \; \Delta T$$

The apparatus most often used for calorimetric measurements is a calorimeter – in your lab this was simply polystyrene coffee cup (see slide).
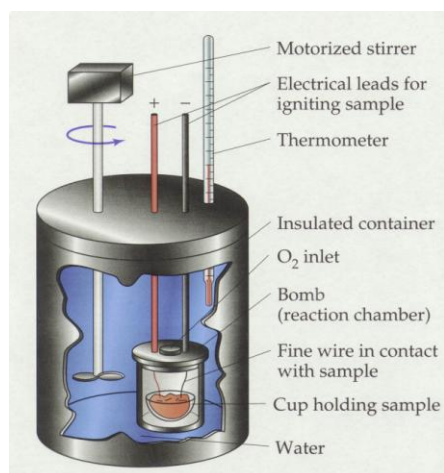
Calorimeter: *"Device used to measure the heat absorbed or evolved during chemical or physical change"*

Discussion: Can any container be used as a calorimeter? What is required of a vessel that is to be used as a calorimeter?

Types of calorimeter (see Appendix)

'Coffee cup' calorimeter (solutions)   'Bomb' calorimeter (gasses / solids)

Note: For a bomb calorimeter, the 'math' is slightly different, as the apparatus as a whole absorbs the heat evolved from the reaction. Thus:

$$q_{(solution)} = C_{cal} \ \Delta T$$

Where: C_{cal} is the heat capacity (in J/°C or kJ/°C) of the calorimeter itself

Hess' Law – Theoretical Determination of Heats of Reaction (ΔH)

Overview: We will learn and implement some familiar math to find ΔH for reactions of interest – this is Hess' Law.

Important fact: Enthalpy is an example of a **State Function** (see appendix / slide). This fact makes the math possible.

Enthalpy as a state function: *'It doesn't matter how you get there - it takes the same amount of energy* (ΔH) *whatever route is taken'*

Example: consider the following number lines, which represent enthalpy changes during chemical reaction(s)

1.

2.

In each case ΔH is the same, irrespective of the route taken. This is of use, since we can find an unknown ΔH$_{rxn}$ from established values – this is Hess's law of Heat summation

Hess's law of Heat summation: *For a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall reaction equals the sum of the enthalpy changes for the individual steps*

'Faulty water heater' example: Find ΔH_{rxn} for the following:

$$2\ C\ (graphite) +\ O_2\ (g)\ \rightarrow\ 2\ CO\ (g);\ \Delta H_{rxn} = ?$$
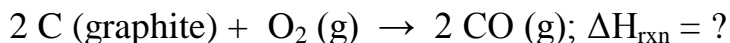
Given:

1. $2\ C\ (graphite) + 2\ O_2\ (g)\ \rightarrow\ 2\ CO_2\ (g);\ \ \Delta H_1 = -787\ kJ$

2. $2\ CO_2\ (g)\ \rightarrow\ 2\ CO\ (g) +\ O_2\ (g)\ );\ \ \Delta H_2 = +566\ kJ$ $+$

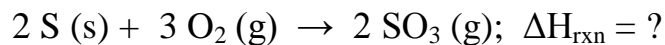**Since the desired reaction is the sum of reactions 1 and 2, then $\Delta H_{rxn} = \Delta H_1 + \Delta H_2$**
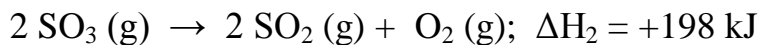
Manipulating Thermochemical equations

Sometimes just adding known thermochemical equations does not give the desired unknown thermochemical equation. The known thermochemical equations can be 'worked over' by following these rules:

ADD REACTIONS : ADD ΔHs
SUBTRACT REACTIONS : SUBTRACT ΔHs
MULTIPLY REACTION : MULTIPLY ΔH
REVERSE REACTION : MULTIPLY ΔH x (-1)

<u>Worked Example</u>: Find ΔH_{rxn} for the following:

$$2 \text{ S (s)} + 3 \text{ O}_2 \text{ (g)} \rightarrow 2 \text{ SO}_3 \text{ (g)}; \ \Delta H_{rxn} = ?$$

<u>Given</u>:

$$\text{S (s)} + \text{O}_2 \text{ (g)} \rightarrow \text{SO}_2 \text{ (g)}; \ \Delta H_1 = \text{-297 kJ}$$

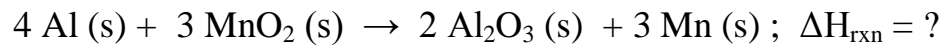$$2 \text{ SO}_3 \text{ (g)} \rightarrow 2 \text{ SO}_2 \text{ (g)} + \text{O}_2 \text{ (g)}; \ \Delta H_2 = +198 \text{ kJ}$$
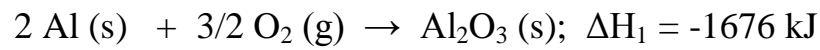
~Always follow this procedure:

1. Arrange the known reaction(s) so reactant(s) and product(s) common to the unknown reaction appear on the 'correct' sides.

2. Multiply known reaction(s) so similar amounts of reactants and products, common to the unknown reaction, appear on the 'correct' sides.

3. Add known reactions – their product should similar to the unknown

Task: Calculate ΔH_{rxn} for:

$$4 \text{ Al (s)} + 3 \text{ MnO}_2 \text{ (s)} \rightarrow 2 \text{ Al}_2\text{O}_3 \text{ (s)} + 3 \text{ Mn (s)} ; \quad \Delta H_{rxn} = ?$$

Given:

$$2 \text{ Al (s)} + 3/2 \text{ O}_2 \text{ (g)} \rightarrow \text{Al}_2\text{O}_3 \text{ (s)}; \quad \Delta H_1 = -1676 \text{ kJ}$$

$$\text{Mn (s)} + \text{O}_2 \text{ (g)} \rightarrow \text{MnO}_2 \text{ (s)} \quad \Delta H_2 = -521 \text{ kJ}$$

	Standard Heats of Formation (ΔH_f)
	Idea / Analogy: Establish a 'spelling bee champion vocabulary' of known enthalpies (standard heats of formation, ΔH_f) from which any 'sentence' (reaction) can be constructed.

Analogy: The following two short 'sentences' (reactions) can be combined to give the required 'longer sentence' (equation):

> *The cat sat*
>
> *on the mat   +*
> _____
>
>   *The cat sat on the mat*

Recall: This is how our previous Hess' Law examples have worked to this point. However, the two small 'sentences' can *only* be combined to make the final *The cat sat on the mat* sentence. This is somewhat limiting, as other new sentences cannot be constructed.

However, having a large vocabulary (knowing lots of words) means virtually ant new sentence can be constructed, for example *Mat sat on the cat!* Standard heats of formation are the chemical equivalent of words in our analogy

Definition of Standard Heats (Enthalpies) of Formation (ΔH_f)

The enthalpy change (kJ/mol) for the formation of one mole of a substance in its standard state (i.e. its physical state at 1.00 atm, 25°C) from its elements in their standard states.

Example: H_2 (g)   + $\frac{1}{2}$ O_2 (g) $\rightarrow$ H_2O (l) ; ΔH_f = -285.8 kJ

Discussion: Some heats of formation have zero values. Why is this? See Appendices here & you're text for a full list

Simple worked example: What is the heat of vaporization, ΔH_{vap} (the energy needed to convert 1 mole of liquid substance to one mole of gaseous substance at its boiling point) for:

$$CS_2(l) \rightarrow CS_2(g); \Delta H_{vap} = ?$$

Where: $\Delta H_f CS_2(l) = +87.9$ kJ and $\Delta H_f CS_2(g) = +117$ kJ
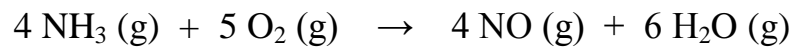
Graphical method

Formula method

Task: calculate the heat of vaporization for water. What is the heat of vaporization for 2 moles of water?

Where: ΔH_f $H_2O(l)$ = -285.8 kJ and ΔH_f H_2O (g) = -241.8 kJ

ANS = 44 kJ

<u>Harder worked example</u>: calculate ΔH_{rxn} for:

$$4\ NH_3\ (g)\ +\ 5\ O_2\ (g)\ \rightarrow\ 4\ NO\ (g)\ +\ 6\ H_2O\ (g)$$

<u>Given</u>: ΔH_f NH_3 (g) = -45.9 kJ
                      ΔH_f NO (g) = +90.3 kJ
                      ΔH_f H_2O (g) = -241.8 kJ

<u>Group Task</u>: calculate ΔH_{rxn} for:

$$2 \text{ PbS (s)} + 3 \text{ O}_2 \text{ (g)} \rightarrow 2 \text{ SO}_2 \text{ (g)} + 2 \text{ PbO (s)}$$
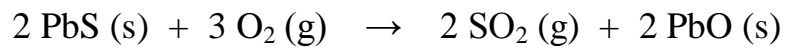
<u>Given</u>: ΔH_f PbS (s) = -98.3 kJ
ΔH_f SO$_2$ (g) = -296.8 kJ
ΔH_f PbO (s) = -219.0 kJ

ANS = -835.6

Appendix: The Strength of Covalent Bonds (Bond Enthalpies)

Background: Enthalpy the *energy* (in kJ) required to break one *mole* of a specified type of bond. Units are kJ/mole. For Cl_2:

$$:\ddot{C}l-\ddot{C}l: \quad \rightarrow \quad :\ddot{\dot{C}}l: \quad + \quad :\ddot{\dot{C}}l: \quad ; \Delta H = 242 \text{ kJ/mol}$$

i.e. it tales 242 kJ of energy to break one mole of Cl-Cl bonds

Some Average Single- and Multiple-Bond Energies*

Single Bonds

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	414	389	464	569	293	318	339	431	368	297
C		347	293	351	439	289	264	259	330	276	238
N			159	201	272		209		201	243?	
O				138	184	368	351		205		201
F					159	540	490	285	255	197?	
Si						176	213	226	360	289	
P							213	230	331	272	213
S								213	251	213	
Cl									243	218	209
Br										192	180
I											151

Multiple Bonds

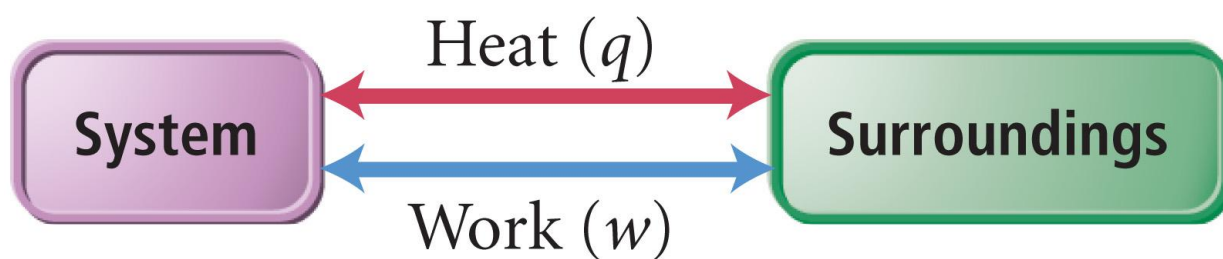|			
N=N	418	C=C	611
N≡N	946	C≡C	837
N=O	590	C=O (in O=C=O)	803
C≡N	891	C=O (as in H_2C=O)	745
O=O (in O_2)	498	C≡O	1075

*In kilojoules per mole.

A State Function
Change in altitude depends only on the difference between the initial and final values, not on the path taken.
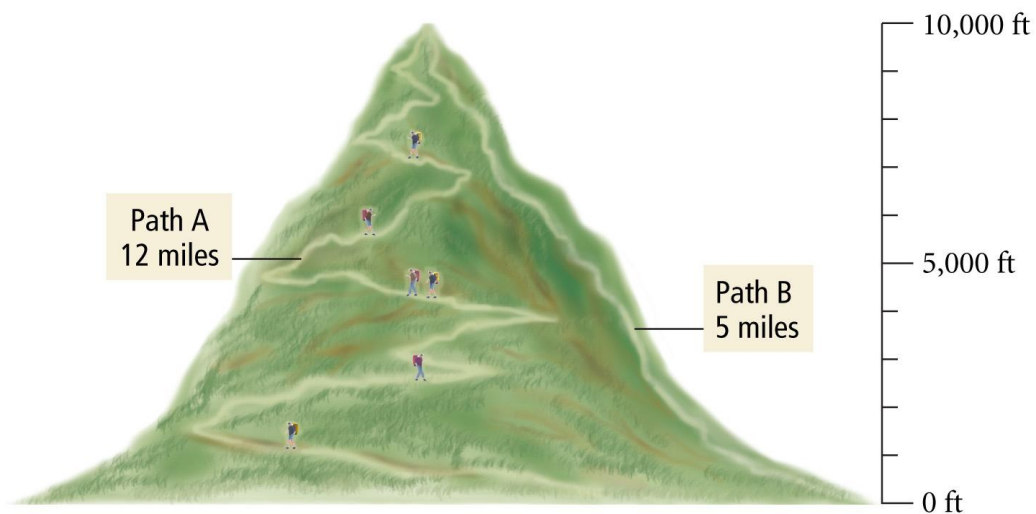
Path A
12 miles

Path B
5 miles

10,000 ft

5,000 ft

0 ft

Heat (q)
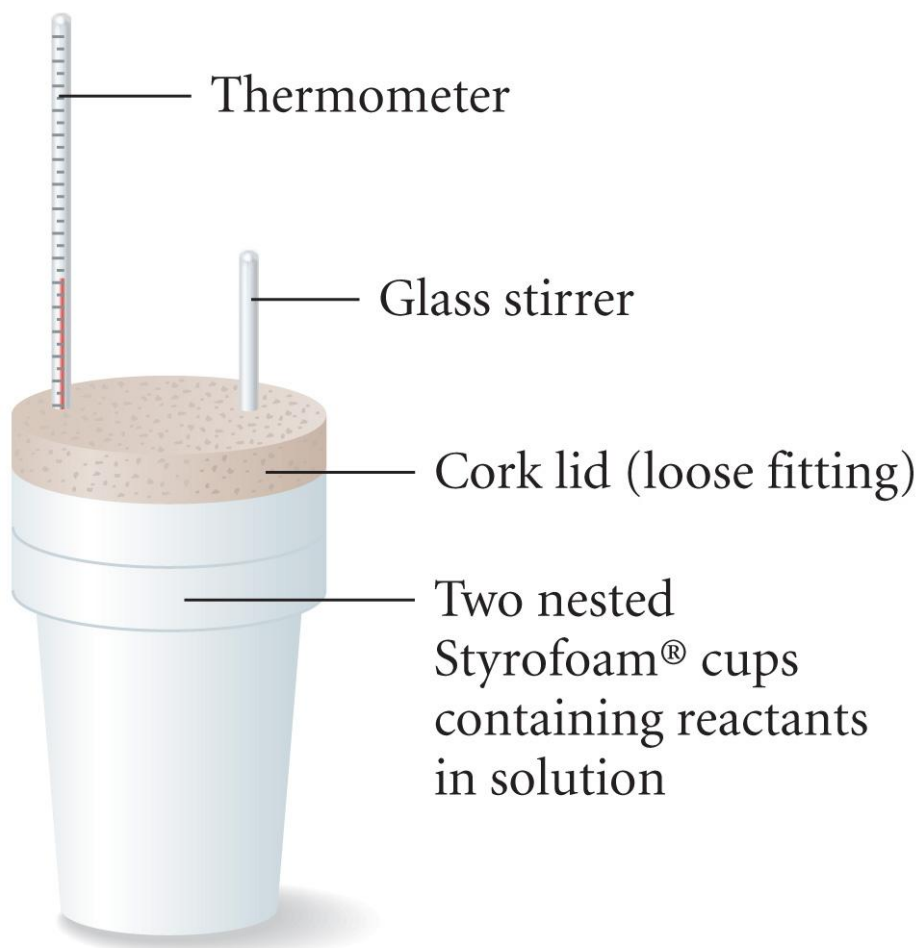
System

Surroundings

Work (w)

TABLE 6.5 Standard Enthalpies of Formation, ΔH_f°, at 298 K

Formula	ΔH_f° (kJ/mol)	Formula	ΔH_f° (kJ/mol)	Formula	ΔH_f° (kJ/mol)
Bromine		$C_3H_8O(l, \text{isopropanol})$	−318.1	*Oxygen*	
$Br(g)$	111.9	$C_6H_6(l)$	49.1	$O_2(g)$	0
$Br_2(l)$	0	$C_6H_{12}O_6(s, \text{glucose})$	−1273.3	$O_3(g)$	142.7
$HBr(g)$	−36.3	$C_{12}H_{22}O_{11}(s, \text{sucrose})$	−2226.1	$H_2O(g)$	−241.8
				$H_2O(l)$	−285.8
Calcium		*Chlorine*		*Silver*	
$Ca(s)$	0	$Cl(g)$	121.3	$Ag(s)$	0
$CaO(s)$	−634.9	$Cl_2(g)$	0	$AgCl(s)$	−127.0
$CaCO_3(s)$	−1207.6	$HCl(g)$	−92.3	*Sodium*	
Carbon		*Fluorine*		$Na(s)$	0
$C(s, \text{graphite})$	0	$F(g)$	79.38	$Na(g)$	107.5
$C(s, \text{diamond})$	1.88	$F_2(g)$	0	$NaCl(s)$	−411.2
$CO(g)$	−110.5	$HF(g)$	−273.3	$Na_2CO_3(s)$	−1130.7
$CO_2(g)$	−393.5			$NaHCO_3(s)$	−950.8
$CH_4(g)$	−74.6	*Hydrogen*		*Sulfur*	
$CH_3OH(l)$	−238.6	$H(g)$	218.0	$S_8(s, \text{rhombic})$	0
$C_2H_2(g)$	227.4	$H_2(g)$	0	$S_8(s, \text{monoclinic})$	0.3
$C_2H_4(g)$	52.4	*Nitrogen*		$SO_2(g)$	−296.8
$C_2H_6(g)$	−84.68	$N_2(g)$	0	$SO_3(g)$	−395.7
$C_2H_5OH(l)$	−277.6	$NH_3(g)$	−45.9	$H_2SO_4(l)$	−814.0
$C_3H_8(g)$	−103.85	$NH_4NO_3(s)$	−365.6		
$C_3H_6O(l, \text{acetone})$	−248.4	$NO(g)$	91.3		
		$N_2O(g)$	81.6		

The Coffee-Cup Calorimeter

Thermometer

Glass stirrer

Cork lid (loose fitting)

Two nested
Styrofoam® cups
containing reactants
in solution

The Bomb Calorimeter

Thermometer

Ignition wire

Stirrer

Water

Tightly sealed "bomb"

Sample

Oxygen

$$q = C \times \Delta T$$

Heat capacity

TABLE 6.4 Specific Heat Capacities of Some Common Substances

Substance	Specific Heat Capacity, C_s (J/g·°C)*
Elements	
Lead	0.128
Gold	0.128
Silver	0.235
Copper	0.385
Iron	0.449
Aluminum	0.903
Compounds	
Ethanol	2.42
Water	4.18
Materials	
Glass (Pyrex)	0.75
Granite	0.79
Sand	0.84

*At 298 K.