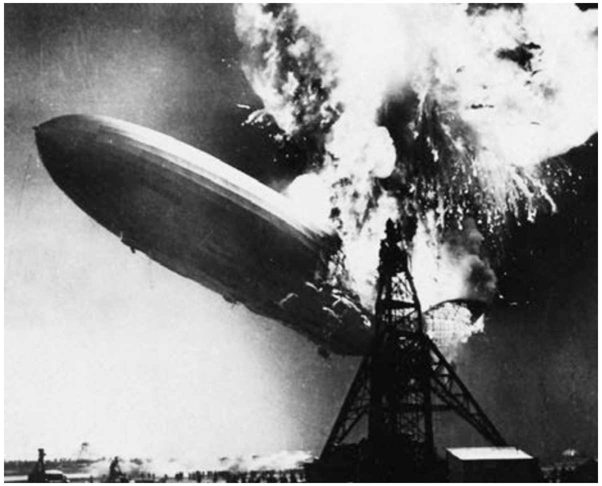
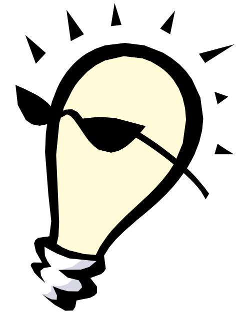


Thermochemistry

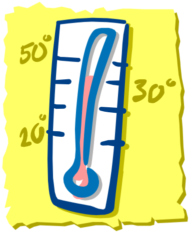
<u>***Energy*** is the capacity to do work</u>



- ***Thermal energy*** is the energy associated with the random motion of atoms and molecules
- ***Chemical energy*** is the energy stored within the bonds of chemical substances
- ***Nuclear energy*** is the energy stored within the collection of neutrons and protons in the atom
- ***Electrical energy*** is the energy associated with the flow of electrons
- ***Potential energy*** is the energy available by virtue of an object's position

Energy Changes in Chemical Reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.



Temperature is a measure of the **thermal energy**.

Temperature ≠ Thermal Energy

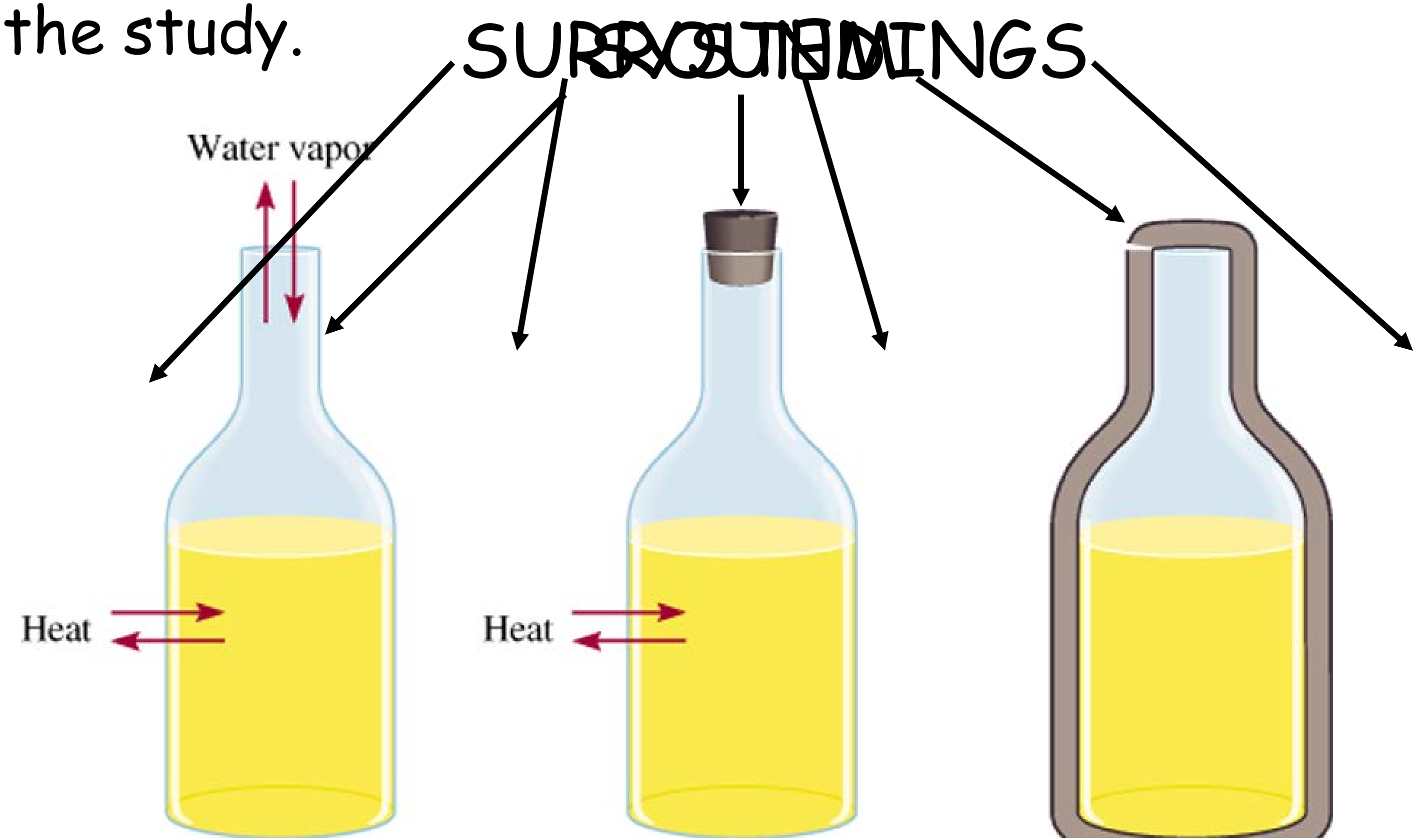
$90^{0}C$

$40^{0}C$

greater thermal energy

Thermochemistry is the study of heat change in chemical reactions.

The ***system*** is the specific part of the universe that is of interest in the study.



open closed isolated

Exchange: mass & energy energy nothing

Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) + \text{energy}$$

$$H_2O(g) \longrightarrow H_2O(l) + \text{energy}$$

Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

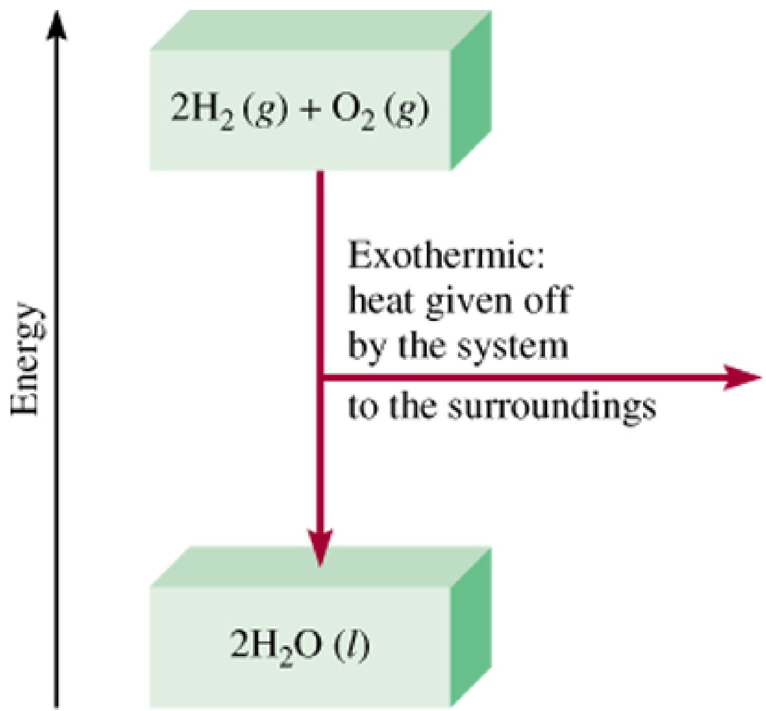
$$\text{energy} + 2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$$

$$\text{energy} + H_2O(s) \longrightarrow H_2O(l)$$

Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

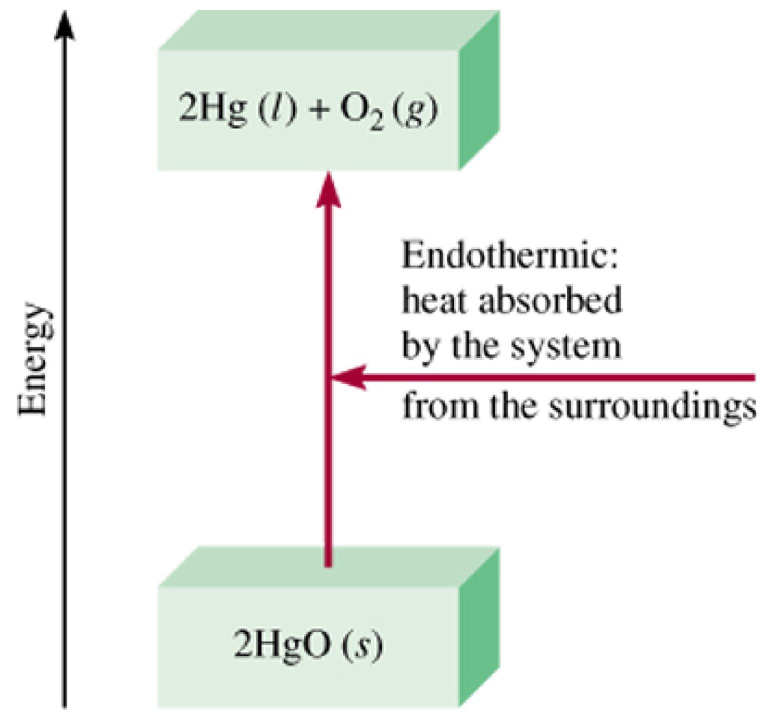
$$DH = H\,(\text{products}) - H\,(\text{reactants})$$

DH = heat given off or absorbed during a reaction **at constant pressure**



$H_{products} < H_{reactants}$

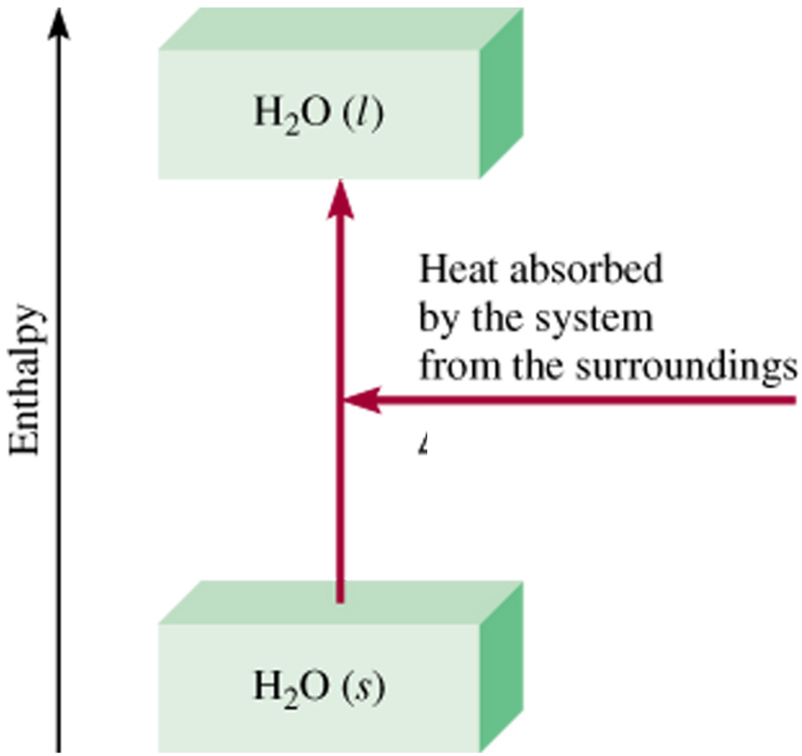
$DH < 0$



$H_{products} > H_{reactants}$

$DH > 0$

Thermochemical Equations



Is D*H* negative or positive?

System absorbs heat

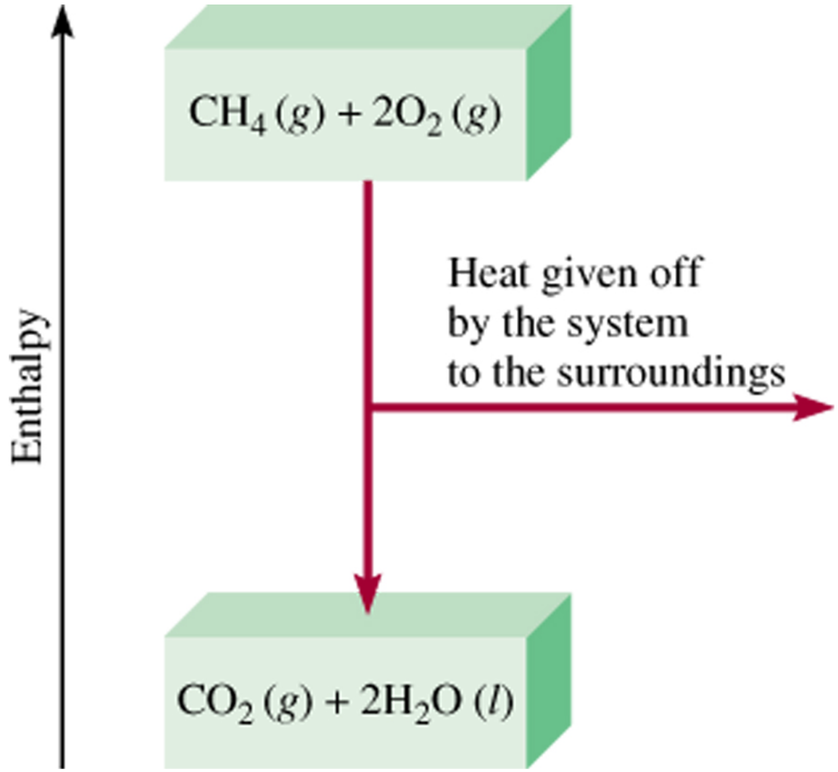
Endothermic

D*H* > 0

6.01 kJ are absorbed for every 1 mole of ice that melts at 0^0C and 1 atm.

H_2O (*s*) ⟶ H_2O (*l*) D*H* = 6.01 kJ

Thermochemical Equations



Is Δ*H* negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

890.4 kJ are released for every 1 mole of methane that is combusted at 25^0C and 1 atm.

$$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l) \quad \Delta H = -890.4\ \text{kJ}$$

Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance

$$H_2O\ (s) \longrightarrow H_2O\ (l) \quad DH = 6.01\ \text{kJ}$$

- If you reverse a reaction, the sign of D*H* changes

$$H_2O\ (l) \longrightarrow H_2O\ (s) \quad DH = -6.01\ \text{kJ}$$

- If you multiply both sides of the equation by a factor *n*, then D*H* must change by the same factor *n*.

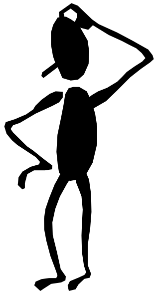
$$2H_2O\ (s) \longrightarrow 2H_2O\ (l) \quad DH = 2 \times 6.01 = 12.0\ \text{kJ}$$

Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.

$$H_2O\,(s) \longrightarrow H_2O\,(l) \quad DH = 6.01\text{ kJ}$$

$$H_2O\,(l) \longrightarrow H_2O\,(g) \quad DH = 44.0\text{ kJ}$$



How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?

$$P_4\,(s) + 5O_2\,(g) \longrightarrow P_4O_{10}\,(s) \quad DH = -3013\text{ kJ}$$

$$266\text{ g } P_4 \times \frac{1\text{ mol } P_4}{123.9\text{ g } P_4} \times \frac{3013\text{ kJ}}{1\text{ mol } P_4} = 6470\text{ kJ}$$

The ***specific heat*** (*s*) of a substance is the amount of heat (*q*) required to raise the temperature of **one gram** of the substance by **one degree** Celsius.

The ***heat capacity*** (*C*) of a substance is the amount of heat (*q*) required to raise the temperature of **a given quantity** (*m*) of the substance by **one degree** Celsius.

Table 6.1 The Specific Heats of Some Common Substances

Substance	Specific heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184
C_2H_5OH (ethanol)	2.46

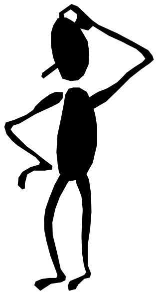
$$C = ms$$

<u>Heat (*q*) absorbed or released:</u>

$$q = msDt$$

$$q = CDt$$

$$Dt = t_{final} - t_{initial}$$



Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?

Establish an arbitrary scale with the **standard enthalpy of formation** (DH_f^0) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (DH_f^0) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.

The standard enthalpy of formation of any element in its most stable form is zero.

$DH_f^0(O_2) = 0$

DH_f^0 (C, graphite) = 0

$DH_f^0(O_3) = 142$ kJ/mol

DH_f^0 (C, diamond) = 1.90 kJ/mol

The **standard enthalpy of reaction** (DH^0_{rxn}) is the enthalpy of a reaction carried out at 1 atm.

$$aA + bB \longrightarrow cC + dD$$

$$DH^0_{rxn} = [cDH^0_f(C) + dDH^0_f(D)] - [aDH^0_f(A) + bDH^0_f(B)]$$

$$DH^0_{rxn} = SnDH^0_f\ (products) - SmDH^0_f\ (reactants)$$

Hess's Law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)

The ***enthalpy of solution*** (*DH*$_{soln}$) is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

$$DH_{soln} = H_{soln} - H_{components}$$

Table 6.4 Heats of Solution of Some Ionic Compounds

Compound	ΔH_{soln} (kJ/mol)	
LiCl	−37.1	exothermic
$CaCl_2$	−82.8	exothermic
NaCl	4.0	endothermic
KCl	17.2	endothermic
NH_4Cl	15.2	endothermic
NH_4NO_3	26.2	endothermic

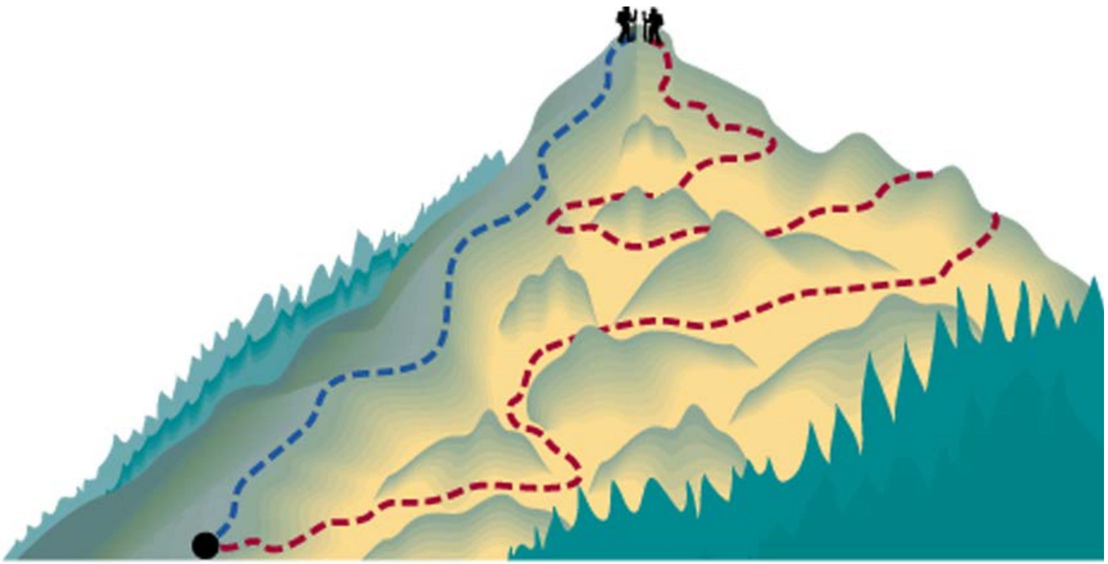
Which substance(s) could be used for melting ice?

Which substance(s) could be used for a cold pack?

Thermodynamics

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, pressure, volume, temperature



Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.

Thermodynamics

$DE = q + w$

DE is the change in internal energy of a system

q is the heat exchange between the system and the surroundings

w is the work done on (or by) the system

$w = -PDV$ when a gas expands against a constant external pressure

Table 6.5 Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	−
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	−