Internal Energy of a System

O The **internal energy** of a chemical system is its total energy, which is the sum of the potential and kinetic energies of the substances in it:

$$E = K_s + U_s$$

P U_s comes from the attractions and repulsions among all the particles (atoms, molecules, subatomic particles) of which the substances are composed.

P K_s comes from the motions of all those particles.

O Absolute values of E, K_s, and U_s cannot be determined in general.

O In general, only changes in energy, ΔE, can be measured:

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{f}} - E_{\text{i}}$$

K By the First Law of Thermodynamics, the only way the energy of the system can change is through interaction with the surroundings.

Transferring Heat and Doing Work

- A system undergoing chemical or physical change can change its internal energy by transferring **heat (*q*)**, doing **work (*w*)**, or both:

$$\Delta E = q + w$$

- The system can do work on the surroundings or vice versa, indicated by the sign on *w*:

  $w < 0$ system does work on surroundings

  $w > 0$ surroundings do work on system

- One specific way in which a chemical system can do work is through the expansion or contraction of a gas against a constant external pressure. This results in a change of volume, ΔV, from which the work can be calculated as

$$w = -P@\Delta V$$

Heat Change and Enthalpy

O As a chemical or physical change occurs, potential energy changes by gaining or losing heat, resulting in a temperature change.

- P This change in heat content is sometimes called the **heat of reaction**.

O We will often be interested in the *heat content under constant pressure conditions*, called the **enthalpy**, *H*, of the system.

- P *H* cannot be measured directly, but we can measure the change in *H*, defined as

$$\Delta H \; / \; H_f - H_i = q_P$$

Enthalpy and Internal Energy

- Under constant pressure conditions, we can rewrite the defining equation for internal energy as

$$\Delta E = \Delta H + w$$

from which it follows

$$\Delta H = \Delta E - w$$

  - In other words, the enthalpy change is that portion of the change in internal energy due to heat change under constant pressure.
  - If no work is done ($w = 0$), then

$$\Delta H = \Delta E$$

Factors Determining the Value of Δ*H*

O The amount of heat transferred in a chemical or physical process depends upon

- P physical conditions
- P amount of substances
- P direction of change

O The *physical conditions* on which enthalpy depends are

- P temperature (*T*)
- P pressure (*P*)
- P physical state (i.e., solid, liquid, gas).

K Therefore, we must be careful when quoting values of q or ΔH to be sure to specify these conditions.

Standard Conditions

O **Standard conditions** are defined as

- P T = 25ºC = 298.15 K
- P P = 1 atm = 760 mm Hg = 29.9213 in. Hg
- P all substances in their usual states for these conditions (the **standard state**).

K The enthalpy change of a process under standard conditions, called the **standard enthalpy**, is designated $\Delta \boldsymbol{H}^{o}$.

Thermochemical Equations

- A thermochemical equation is an ordinary chemical equation written in conjunction with a thermochemical value (e.g., *q*, Δ*H*), where the reactant and product coefficients are taken as numbers of moles.

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H^o = -286 \text{ kJ/mol}$$

  - Under standard conditions, 286 kJ is liberated when one mole of liquid water is formed from one mole of hydrogen gas and one-half mole of oxygen gas.

  - When the value of the enthalpy is quoted for the reaction occurring under standard conditions, it is called the **standard enthalpy**, symbolized ΔH^o

ΔH and State

Standard conditions (T = 25ºC, P = 1 atm)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H^o = -286$ kJ/mol

L All conditions of standard state met.

Non-standard conditions (T = 25ºC, P = 1 atm)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta H = -242$ kJ/mol

L Gaseous water is not the standard state.

Non-standard conditions (T = 50ºC, P = 1 atm)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta H = -241$ kJ/mol

L T = 50ºC is not the standard state.

ΔH and Amount

$H_2(g) + ½O_2(g)$ 6 $H_2O(l)$ $\Delta H^o = –286$ kJ

$2H_2(g) + O_2(g)$ 6 $2H_2O(l)$ $\Delta H^o = –572$ kJ

ΔH and Direction

$H_2(g) + ½O_2(g)$ 6 $H_2O(l)$ $\Delta H^o = –286$ kJ/mol

$H_2O(l)$ 6 $H_2(g) + ½O_2(g)$ $\Delta H^o = +286$ kJ/mol