

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:

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_f - E_i$$

- 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

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

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

from which it follows

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

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

$$\Delta H = \Delta E$$

Factors Determining the Value of ΔH

- 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.

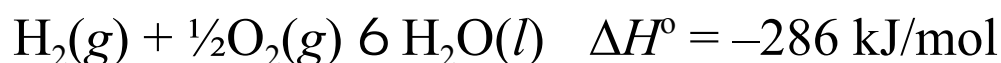
Standard Conditions

- O **Standard conditions** are defined as
 - P $T = 25^{\circ}\text{C} = 298.15\text{ K}$
 - P $P = 1\text{ atm} = 760\text{ mm Hg} = 29.9213\text{ in. Hg}$
 - 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 ΔH° .

Thermochemical Equations

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



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

ΔH and State

Standard conditions ($T = 25^\circ\text{C}$, $P = 1 \text{ atm}$)



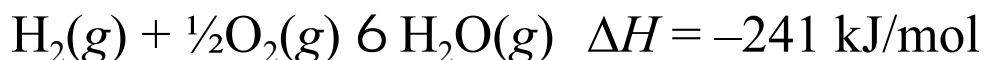
L All conditions of standard state met.

Non-standard conditions ($T = 25^\circ\text{C}$, $P = 1 \text{ atm}$)



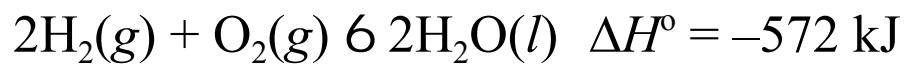
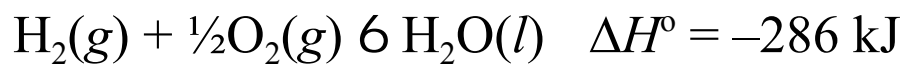
L Gaseous water is not the standard state.

Non-standard conditions ($T = 50^\circ\text{C}$, $P = 1 \text{ atm}$)



L $T = 50^\circ\text{C}$ is not the standard state.

ΔH and Amount



ΔH and Direction

