

THERMODYNAMICS

- Thermodynamics is concerned with the energy changes that accompany chemical and physical processes.
- Two conditions must be fulfilled in order to observe a chemical or physical change:
 1. The change must be possible (determined by Thermodynamics)
 2. The change must occur at a reasonable speed (determined by Kinetics)

Important Terms in Thermodynamics:

1. System and Surroundings:

- (a) System : The part of the universe we happen to be studying
- (b) Surroundings: Everything outside the system
- (c) State of the system: fixed properties of the:

System	Components of the system
<ul style="list-style-type: none"> • Temperature • Pressure 	<ul style="list-style-type: none"> • Number of moles • Physical State of each system

2. Adiabatic and Isothermal Changes:

Adiabatic Change	Isothermal Change
<ul style="list-style-type: none"> • Takes place in a system that is insulated from the surroundings. • Heat cannot flow between system and surroundings. • The temperature of the system changes: <ul style="list-style-type: none"> ➤ Temp. increases if rxn is exothermic. ➤ Temp. decreases if rxn is endothermic 	<ul style="list-style-type: none"> • Takes place in a system that is not insulated from the surroundings. • Heat can flow between system and surroundings and as such the temperature can be maintained constant. • A change that occurs at constant temperature.

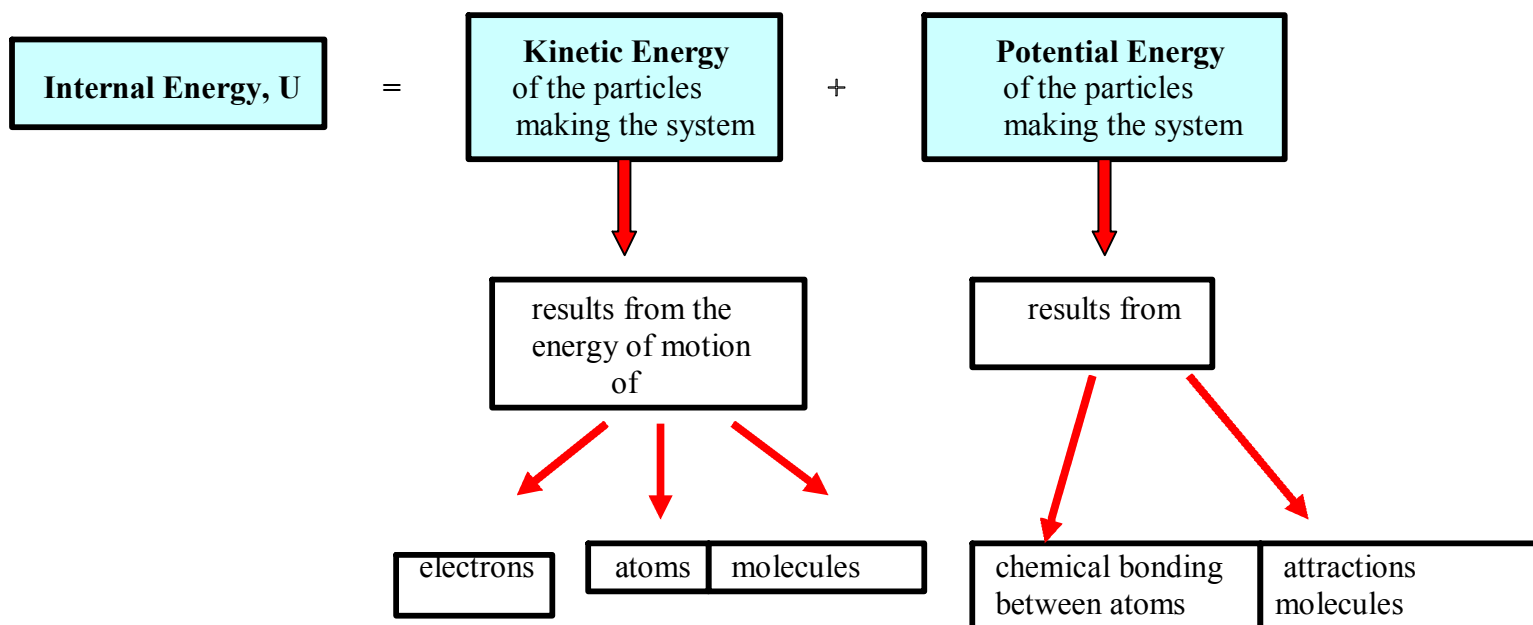
3. State Function

- A quantity whose value depends only on the current state of the system, and does not depend on the prior history of the system.

Example: Temperature, Internal Energy

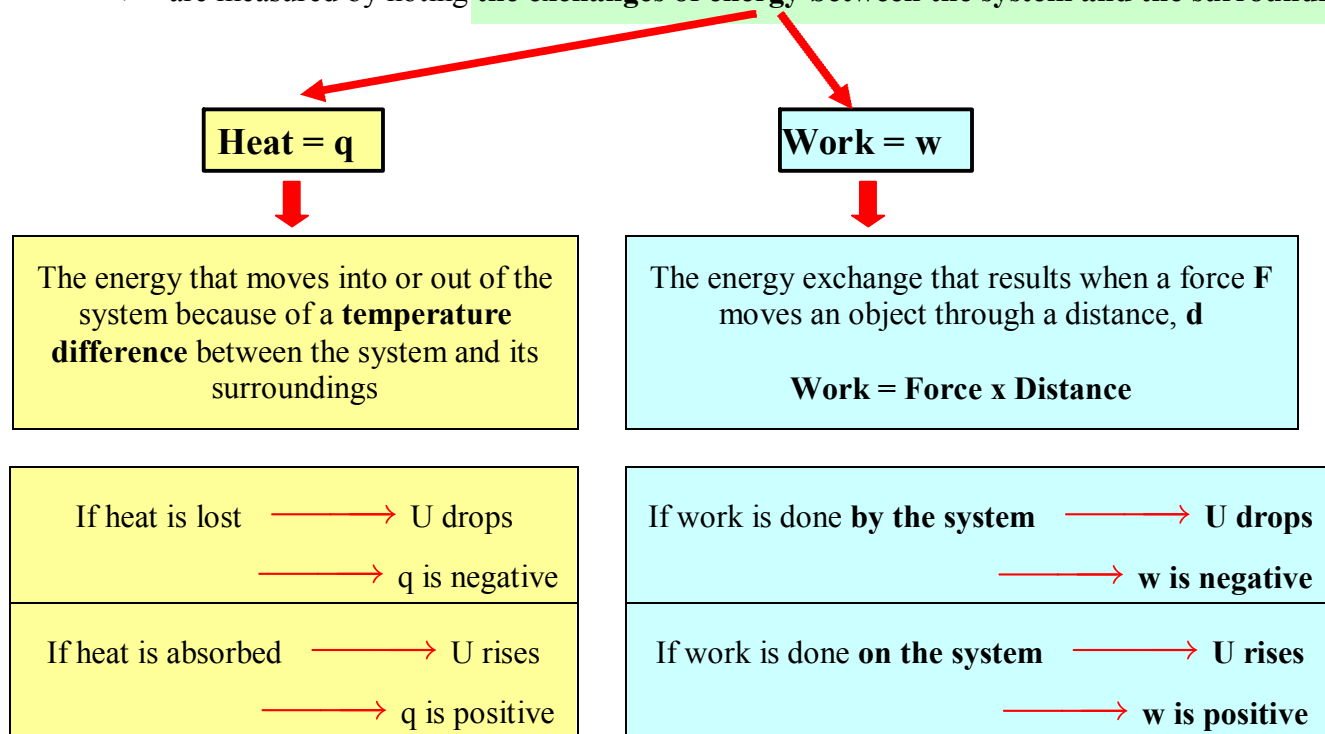
4. Internal Energy

- Internal Energy (U) is a **state function**.
- It is a property of a system that depends only on its present state, determined by variables such as temperature and pressure



FIRST LAW OF THERMODYNAMICS

- The 1st Law of Thermodynamics is the “Law of Conservation of Energy” applied to thermodynamic systems.
- When a system changes from one state to another (ex: warming), its internal energy changes from one definite energy to another.
- Change in Internal Energy : $\Delta U = U_f - U_i$ where: U_f = final value of the internal energy
 U_i = initial value of the internal energy
- The Changes in Internal Energy, ΔU :
 - are more important in thermodynamics than the absolute values of Internal Energy
 - are measured by noting **the exchanges of energy between the system and the surroundings**

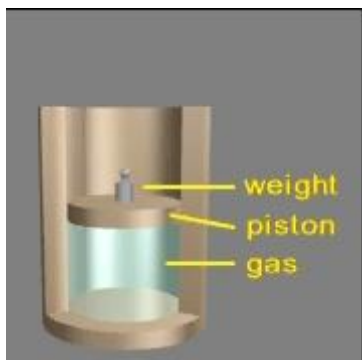


Examples:

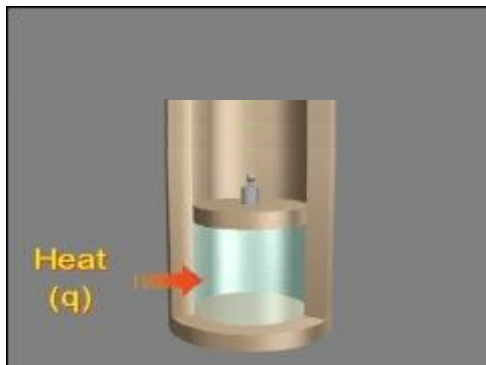
Determine the sign of the work for each of the changes shown below (carried out at constant P):

- a) $2 \text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{SO}_3 (\text{g})$ $w =$
- b) $\text{CaCO}_3 (\text{s}) \rightarrow \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$ $w =$
- c) $\text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l}) + \text{CaCO}_3 (\text{s}) \rightarrow \text{Ca}^{2+} (\text{aq}) + 2 \text{HCO}_3^- (\text{aq})$ $w =$

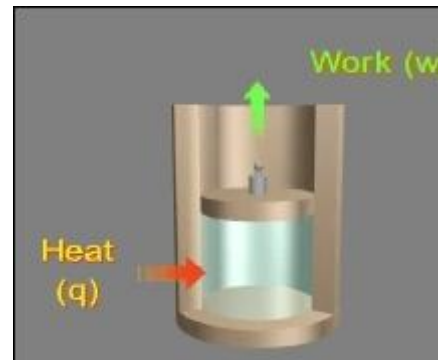
HEAT (q) AND WORK (w) RELATIONSHIP IN A PHYSICAL SYSTEM



A gas is enclosed in a vessel equipped with a movable piston, momentarily fixed in position



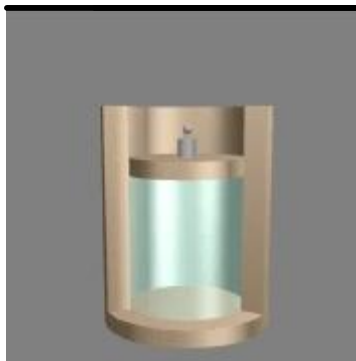
Heat passes from the surroundings to the vessel and the temperature of the gas is increased
Assume $q = + 165 \text{ J}$



The gas pressure increases and causes the gas to expand. This will cause to lift the piston and the weight on top of it



In lifting the weight, the system does work = the energy gained by piston and weight
Assume $w = - 92 \text{ J}$



The system gains Internal Energy, U from the heat absorbed: $q = + 165 \text{ J}$

The system loses internal energy via the work done: $w = - 92 \text{ J}$

The change in Internal Energy of the System = $\Delta U = (+165 \text{ J}) + (- 92 \text{ J}) = + 73 \text{ J}$

FIRST LAW OF THERMODYNAMICS

- The Change in Internal Energy of a system, ΔU , equals $q + w$

$$\Delta U = q + w$$

- Consider a system where work is done on the system and heat is lost by the system:



A gas is enclosed in a vessel equipped with a movable piston, momentarily fixed in position.



Work is done on the system by pushing down the piston and thus compressing the gas.



The gas pressure increases and causes the gas to warm up. This will cause heat to flow out of the system.

Assume $w = +92 \text{ J}$

Assume $q = -165 \text{ J}$

- The system gains Internal Energy, U from the work done on it :
- The system loses internal energy via the heat lost:
- The change in Internal Energy of the System =

$$w = +92 \text{ J}$$

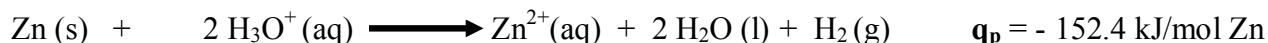
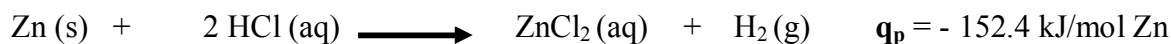
$$q = -165 \text{ J}$$

$$\Delta U = q + w$$

$$\Delta U = (-165 \text{ J}) + (+92 \text{ J}) = -73 \text{ J}$$

Heat (q) and Work (w) relationship in a chemical system

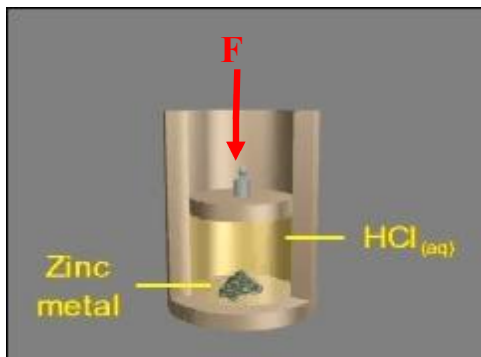
- Consider the following exothermic chemical reaction carried out in a beaker open to the atmosphere:



Note: q_p = indicates that the process occurs at constant pressure (atmospheric pressure)

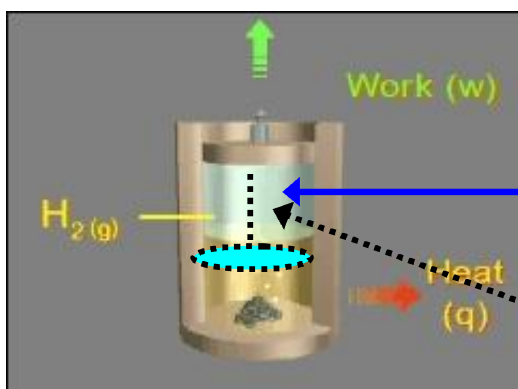
- The H_2 gas that is produced:
 - increases the volume of the system
 - must push against the atmosphere in order to evolve
- It follows that work must be done by the system.
- Can the work done by the system be measured and/or calculated?

PRESSURE-VOLUME WORK



Assume that the pressure exerted by the atmosphere is replaced by a piston and weights, whose downward force of gravity, F , creates a pressure on the gas equivalent to that of the atmosphere

$$F = \text{force of gravity} = \text{atmospheric pressure}$$



ΔV = increase in volume of the system due to the production of H₂ gas

$$\Delta V = (\text{cross sectional area}) \times (\text{height})$$

$$\text{height} = h = \frac{\Delta V}{A}$$

The work done by the system in expanding = (**Force of Gravity**) x (Distance the piston moves)

$$w = -F \times h = -F \times \frac{\Delta V}{A} = -\frac{F}{A} \times \Delta V$$

Atmospheric pressure

- Negative sign is given because work "w" is done by the system and represents energy lost by it.

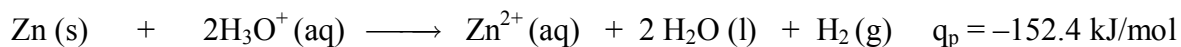
It follows:

$$w = -P \Delta V$$

Examples:

1. If 1.00 mol of Zn reacts with excess hydrochloric acid, 1.00 mol of H₂ is produced. At 25⁰C and 1.00 atm (1.01 x 10² kPa), this amount of H₂ occupies 24.5 L (24.5 L = 24.5 dm³ = 24.5 x 10⁻³ m³). Calculate the change in Internal Energy (ΔU).

$$\Delta U = q_p + w$$



$$q_p = -152.4 \text{ kJ/mol}$$

$$w = ?$$

$$w \text{ done by system to push back atmosphere} = -P\Delta V = -(1.01 \times 10^2 \text{ kPa}) \times (24.5 \times 10^{-3} \text{ m}^3) = -24.7 \text{ kJ}$$

$$w = \text{Expansion Work} = -2.47 \text{ kJ}$$

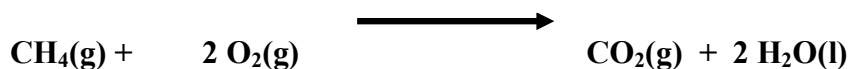
$$\Delta U = q_p + w = (-152.4 \text{ kJ}) + (-2.47 \text{ kJ}) = -154.9 \text{ kJ}$$

- **Conclusion: Energy leaves the system:**
 - mostly as heat ($q_p = -152.4 \text{ kJ}$) and,
 - partly as expansion work (-2.47 kJ)

2. What is ΔU when 1.00 mol of liquid water vaporizes at 100°C?
($\Delta H^0_{\text{vap}} = 40.66 \text{ kJ/mol}$ at 100 °C)

Examples:

3. Consider the combustion (burning) of methane, CH₄, in oxygen:



The heat of reaction at 25 °C and 1.00 atm is -890.2 kJ.

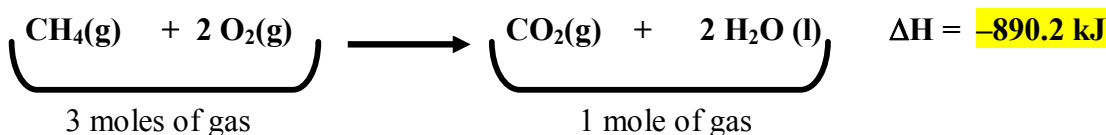
- What is the **change in volume, ΔV** when 1.00 mol CH₄ reacts with 2.00 mol O₂? (Ignore the volume of liquid water formed in the reaction)
- What is **w** for this change?
- Calculate **ΔU** for the change indicated by the chemical equation.

a) **Find the change in volume (ΔV)**

Volume occupied by 1 mole of any gas at STP = 22.41 L

Volume occupied by 1 mole of any of the gases in the equation at 25 °C:

$$V = 22.41 \text{ L} \times \frac{298 \text{ K}}{273 \text{ K}} = 24.46 \text{ L}$$



Gaseous Volume decreases:

3 moles of gas

1 mole of gas

$\Delta V = \text{Volume occupied by 3 moles} - \text{Volume occupied by 1 mole}$

$$\Delta V = (3 \times 24.46 \text{ L}) - 24.46 \text{ L} = 48.92 \text{ L}$$

b) **Calculate the work (w) done on the system**

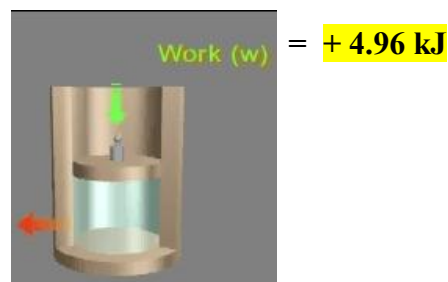
$$w = + P \Delta V = (1.013 \times 10^2 \text{ kPa}) \times (48.92 \times 10^{-3} \text{ m}^3) = 4.96 \text{ kJ}$$

c) **Calculate change in internal energy, ΔU**

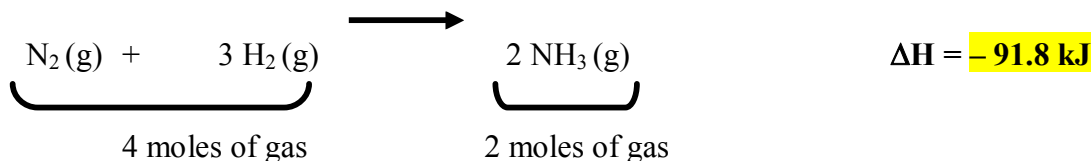
$$q_p = -890.2 \text{ kJ}$$

$$\Delta U = q_p + w = (-890.2 \text{ kJ}) + (+4.96 \text{ kJ}) = \boxed{-885.2 \text{ kJ}}$$

- Conclusion: Energy leaves the system



4. What is ΔU for the following reaction at 25 °C?



- Volume occupied by 1 mole of any of the gases in the equation at 25 °C:

$$V = 22.41 \text{ L} \times \frac{298 \text{ K}}{273 \text{ K}} = 24.46 \text{ L}$$

- The decrease in Volume:

$$\Delta V = 4 \times (24.46 \text{ L}) - 2 \times (24.46 \text{ L}) = 2 \times (24.46 \text{ L}) = 48.924 \text{ L}$$

$$\Delta V = 48.924 \times 10^{-3} \text{ m}^3$$

- Since the Volume decreases, work is done on the chemical system by the atmosphere:

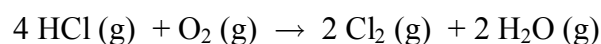
$$w = +P \Delta V = (1.013 \times 10^2 \text{ kPa}) \times (48.924 \times 10^{-3} \text{ m}^3) = +4.956 \text{ kJ}$$

$$\Delta U = q_p + w = (-91.8 \text{ kJ}) + (+4.956 \text{ kJ}) = \boxed{-86.8 \text{ kJ}}$$

- Conclusion: Energy leaves the system

5. Calculate the amount of work done in each of the following reactions. In each case, is the work done **by** or **on** the system?

a) oxidation of HCl at 200 °C



b) The decomposition of NO₂ at 300 °C



ENTHALPY AND ENTHALPY CHANGE

- Recall:

Enthalpy = The Heat of Reaction, ΔH , at constant pressure (q_p)

Actually: **Enthalpy** = $\mathbf{H = U + PV}$

- U (internal Energy), P (pressure), V (volume) are state functions.
- If follows: **H (Enthalpy) is also a state function**

Consequences:

- For a given temperature and pressure, a given amount of a substance has a definite enthalpy.
- If the enthalpies of substances are known, the change of enthalpy for a reaction, ΔH , can be easily calculated.

$\Delta H = \text{Final Enthalpy} - \text{Initial Enthalpy} = H_f - H_i$

At constant pressure, P : $H_f = U_f + PV_f$ **and** $H_i = U_i + PV_i$

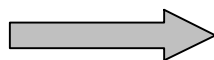
$\Delta H = (U_f + PV_f) - (U_i + PV_i) = (U_f - U_i) + (PV_f - PV_i) = \Delta U + P\Delta V$

$\Delta H = \Delta U + P\Delta V$

and as found earlier: $\Delta U = q_p - P\Delta V$

- It follows: $\Delta H = (q_p - P\Delta V) + P\Delta V = q_p - P\Delta V + P\Delta V = q_p$
- Conclusion: $\mathbf{\Delta H = q_p}$ (Chapter 6)
- The Enthalpy of Reaction equals the Heat of Reaction at constant pressure Applications:

Heat absorbed (endothermic reaction) or given off (exothermic reaction) by a chemical reaction



$\Delta H^0 = \text{Standard Enthalpy Change}$

$\Delta H^0 = \text{Standard Enthalpy Change for a Reaction}$ can be calculated if the Standard Enthalpies of formation, ΔH^0_f for both reactants and products are known.

$\Delta H^0_f = \text{Standard Enthalpy of Formation of a Substance}$
 = Enthalpy change for the formation of one mole of substance in its standard state from its elements in their reference form (most stable form at 25°C and 1.00 atm) and in their standard states. (Given in Table 6.2 and Appendix C)

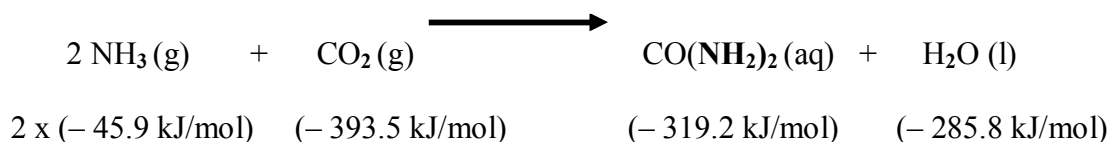
Examples:

1. Calculate the heat absorbed or evolved in the reaction between NH_3 gas and CO_2 gas that yields aqueous urea ($\text{NH}_2\text{—CO—NH}_2$) and liquid water.



From Appendix C:

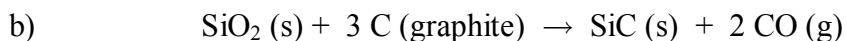
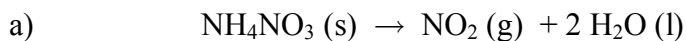
$\Delta H_f^\circ(\text{NH}_3)$	gas	$= -45.9 \text{ kJ/mol}$
$\Delta H_f^\circ(\text{CO}_2)$	gas	$= -393.5 \text{ kJ/mol}$
$\Delta H_f^\circ[\text{CO}(\text{NH}_2)_2]$	aqueous	$= -319.2 \text{ kJ/mol}$
$\Delta H_f^\circ(\text{H}_2\text{O})$	liquid	$= -285.8 \text{ kJ/mol}$



$$\Delta H^\circ = \Sigma n \Delta H_f^\circ(\text{products}) - \Sigma n \Delta H_f^\circ(\text{reactants})$$

$$\Delta H^\circ = [(-319.2) + (-285.8 \text{ kJ})] - [2 \times (-45.9) + (-393.5)] = -119.7 \text{ kJ}$$

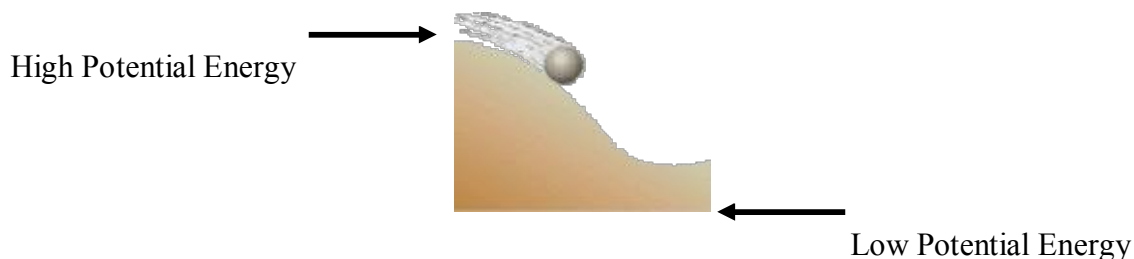
- Since ΔH° is negative, we conclude that the reaction is exothermic.
2. Use data in appendix C to find ΔH° for the reactions shown below:



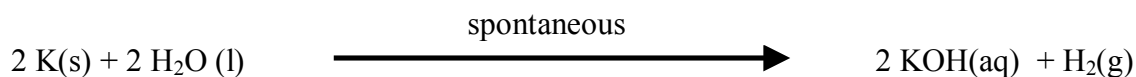
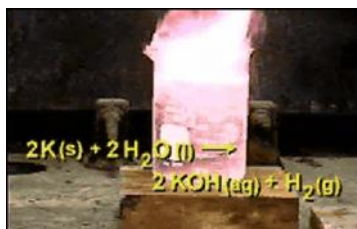
THE SECOND LAW OF THERMODYNAMICS

- **Spontaneous Processes:** Physical or chemical changes that occurs by themselves, without outside assistance

Spontaneous Physical Change: A ball rolling from the top of a hill

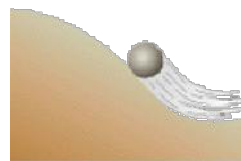


Spontaneous Chemical Change: The reaction of solid K(potassium) with liquid water

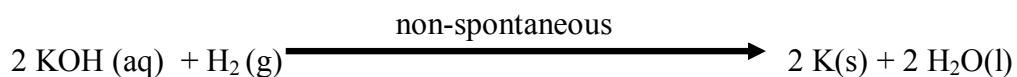


- In order for spontaneous changes to go in the opposite direction work would have to be expended, and the changes would be called non-spontaneous.

Non-spontaneous Physical Change: Rolling a ball uphill



Non-spontaneous Chemical Change: Obtaining K(s) from KOH(aq)



- This process requires several chemical reactions.

NOTE:

- The Second Law of Thermodynamics determines if a reaction is spontaneous or not.
- Exothermic Reactions ($\Delta H < 0$) are not necessarily spontaneous and Endothermic Reactions ($\Delta H > 0$) are not necessarily non-spontaneous

ENTROPY (S)

- Entropy is the thermodynamic quantity that is a measure of the randomness or disorder in a system.
- Entropy is a state function: - the quantity of entropy in a substance depends only on variables that determine the state of the substance (temperature and pressure)
- Entropy is measured in J/K (SI unit)
- Entropy increases when the disorder in a sample of the substance increases:

Example: Consider the melting of ice at 0°C and 1 atm.



ICE

- H₂O molecules occupy regular fixed positions (crystal lattice)
- Ordered crystalline structure

Lower Entropy

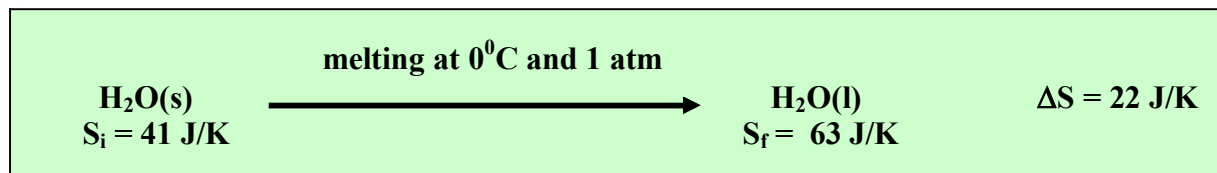
S_i = Initial Entropy
= Entropy of Ice (41 J/K)

LIQUID WATER

- H₂O molecules move about freely, giving a disordered structure
- Less-ordered structure

Higher Entropy

S_f = Final Entropy
= Entropy of liquid water (63 J/K)



- In any natural process the degree of disorder (Entropy) increases.
- Natural processes are changes that occur by themselves (spontaneous changes).

Second Law of Thermodynamics in reference to the system and its surroundings

The Total Entropy of a System and its Surroundings always increases for a Spontaneous Process.

ENTROPY

- is created during a spontaneous change

≠

ENERGY

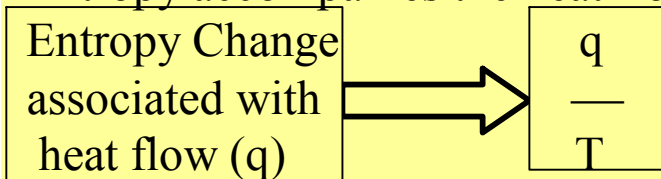
- can be neither created or destroyed during a spontaneous change

SECOND LAW OF THERMODYNAMICS IN REFERENCE TO THE SYSTEM ONLY

- Consider a spontaneous change and the changes that occur in the system at a given temperature:

1. Entropy is created

2. Heat (q) flows into or out of the system
Entropy accompanies the heat flow



$$\Delta S = \text{Entropy created during the spontaneous process}$$

+

$$\text{Change in entropy associated with heat flow}$$

$$\Delta S = \text{Entropy Created}$$

+

$$\text{Entropy Flow}$$

$$\Delta S = \text{Entropy Created}$$

+

$$\frac{q}{T}$$

$$\Delta S = \text{Entropy Created} + \frac{q}{T}$$

For a Spontaneous change:

$$\Delta S > 0$$

$$\text{Entropy Created} > 0$$

$$\frac{q}{T} \rightarrow \text{may be positive or negative}$$

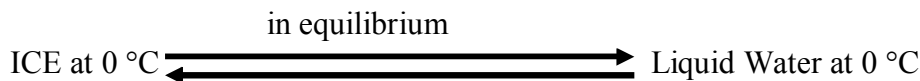
It follows:

$$\Delta S > \frac{q}{T}$$

For a Spontaneous Process at a Given Temperature, the Change in Entropy of the System is greater than the Heat divided by the Absolute Temperature

ENTROPY CHANGE FOR A PHASE TRANSITION

- Consider the melting of ice at 0 °C:



➤ No significant amount of entropy is created

➤ Entropy flow accompanies the heat flow ($q > 0$)

$$\Delta S = \text{Entropy Created} + \frac{q}{T}$$

negligible

- It follows that for an **equilibrium process**:

$$\Delta S = \frac{q}{T}$$

- Note: Most phase changes occur under equilibrium conditions.

Examples:

- Calculate ΔS for the melting of ice (Heat absorbed = Heat of Fusion = $\Delta H_{\text{fus}} = 6.0 \text{ kJ/mol}$)

$$\Delta S = \frac{q}{T} = \frac{6.0 \times 10^3 \text{ J}}{273 \text{ K}} = 22 \text{ J/K}$$

- Liquid ethanol, $\text{C}_2\text{H}_6\text{O} (\text{l})$, at 25°C has an entropy of 161 J/(mol x K). If the heat of vaporization, ΔH_{vap} at 25 °C is 42.3 kJ/mol, what is the entropy of the vapor in equilibrium with the liquid at 25 °C?

When the liquid evaporates, it absorbs heat: $\Delta H_{\text{vap}} = 42.3 \text{ kJ/mol at } 25^\circ\text{C}$

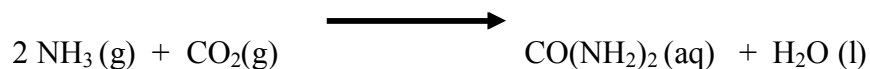
$$\text{Entropy Change} = \Delta S = \frac{q}{T} = \frac{\Delta H_{\text{vap}}}{(25 + 273) \text{ K}} = \frac{42.3 \text{ kJ/mol}}{298 \text{ K}} = 141.9 \text{ J/K x mol}$$

The entropy of 1 mole of vapor is calculated using the entropy of 1 mole of liquid (161 J/K) to which the entropy change resulting from the heat absorption (141.9 J/K) is added:

$$\text{Entropy of Vapor} = 161 \text{ J/K} + 141.9 \text{ J/K} = 303 \text{ J/K } 2^{\text{ND}} \text{ LAW OF}$$

THERMODYNAMICS AND SPONTANEITY OF REACTIONS

- Consider the preparation of urea at constant temperature and pressure:



- Is this a spontaneous reaction? (Does it go from left to right as written?)

- For a spontaneous reaction:
(constant T and P)

$$\Delta S > \frac{q_p}{T} = \frac{\Delta H}{T}$$

$$\Delta S > \frac{\Delta H}{T}$$

- For a spontaneous reaction:
(constant T and P)

$$\frac{\Delta H}{T} - \Delta S < 0$$

smaller larger

- Multiplying each term by the positive quantity T yields:

$$\text{For a spontaneous reaction: } \Delta H - T \Delta S < 0$$

(constant T and P)

- If ΔS is available and ΔH is calculated (Table 6.2), one can predict if the reaction is spontaneous or not:

- $\Delta H - T \Delta S < 0$ The reaction is spontaneous (\longrightarrow)

- $\Delta H - T \Delta S > 0$ The reaction is non-spontaneous (\longrightarrow)

The reaction is spontaneous (\longleftarrow)

- $\Delta H - T \Delta S = 0$ The reaction is at equilibrium (\rightleftharpoons)

- For a spontaneous reaction: $\Delta H - T \Delta S < 0$ (constant T and P)

INTERPRETING SPONTANEITY

- Two factors determine the spontaneity of a chemical change:
 1. **Nature's tendency for the potential energy to be at a minimum.**
 - Any change that tends to lower the potential energy tends to occur spontaneously
 - The quantity that is related to the lowering of the potential energy of changes that take place at constant pressure is ΔH
 - For exothermic reactions $\Delta H < 0$
 - **Exothermic reactions "tend" to occur spontaneously**
 2. **Nature's tendency toward disorder**
 - Any change that tends to increase the disorder of a system tends to occur spontaneously
 - The quantity that is related to the increase in the degree of disorder for changes that take place at constant pressure is ΔS
 - The larger the entropy of a system, the greater its statistical probability
 - **Reactions that go in the direction of greater entropy "tend" to occur spontaneously.**

$$\Delta S = S_{\text{final}} - S_{\text{initial}} \quad \text{When } \Delta S > 0 \quad \text{Spontaneity is favored}$$

- The entropy (S) of a system depends on several factors:
 - (a) Physical state of the components of the system

$$S(\text{solid}) < S(\text{liquid}) < S(\text{gas})$$
 - (b) Temperature of the system

Entropy (S) increases with temperature
 - (c) Mixing of components
 - If the volume of the mixture is larger than the volumes of the components the Entropy (S) increases
 - If two liquids are mixed to form a solution, S increases
 - If two gases are mixed, S increases only if the total volume increases

THIRD LAW OF THERMODYNAMICS

- **A substance that is perfectly crystalline at 0 K has an entropy of zero**
- This law helps determine the Entropy of different substances at different temperatures, if one considers the following facts:
 - When the temperature of a substance is raised from 0 K,
 - the substance absorbs heat, and
 - the substance becomes more disordered
- The entropy change that occurs when heat is absorbed, $\Delta S = \frac{q}{T}$

Examples:

1. What is ΔS for a substance if it is heated from near 0.0 K to 2.0 K and the heat absorbed is 0.19 J?

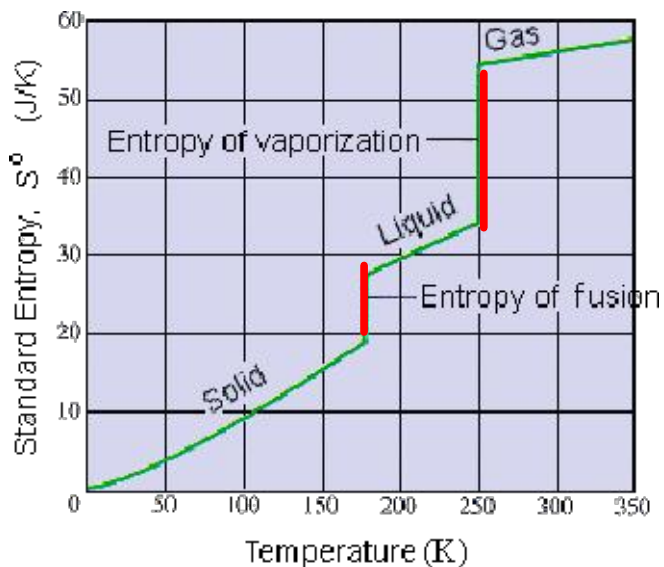
$$\Delta S = \frac{0.19 \text{ J}}{T(\text{average})} = \frac{0.19 \text{ J}}{1.0 \text{ K}} = \mathbf{0.19 \text{ J/K (at 1.0 K)}}$$

2. What is ΔS for the same substance if it is heated from near 2.0 K to 4.0 K and the heat absorbed is 0.88 J?

$$\Delta S = \frac{0.88 \text{ J}}{T(\text{average})} = \frac{0.88 \text{ J}}{3.0 \text{ K}} = \mathbf{0.29 \text{ J/K (at 3.0 K)}}$$

- Proceeding this way, the entropy at any temperature can be determined.

Standard entropy of methyl chloride, CH₃Cl, at various temperatures



Notes:

1. The entropy increases gradually as the temperature increases.
2. The entropy increases sharply when a phase change occurs.

Standard Entropy of a Substance or Ion (Absolute Entropy), S^0

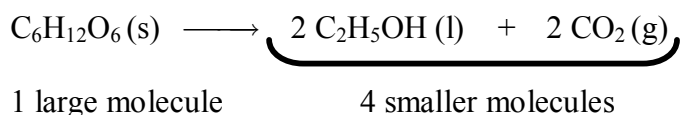
- S^0 is the entropy value for the standard state of the species.
 - For a substance: Standard State is the pure substance at 1 atm
 - For a species in solution: Standard state is the 1 M solution
- S^0 is temperature dependent; it is usually given for 25 °C

Entropy Changes (ΔS) for a Reaction

A. ΔS can sometimes be predicted

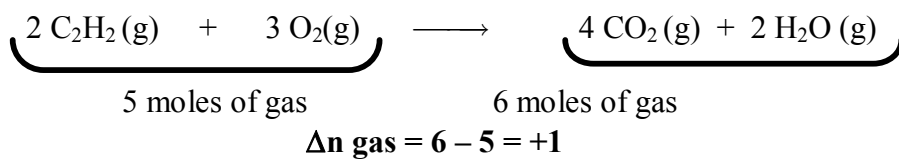
- The entropy usually increases in the following situations:
 - A reaction in which a molecule is broken into two or more smaller molecules.

Example: fermentation of glucose (grape sugar) to alcohol:

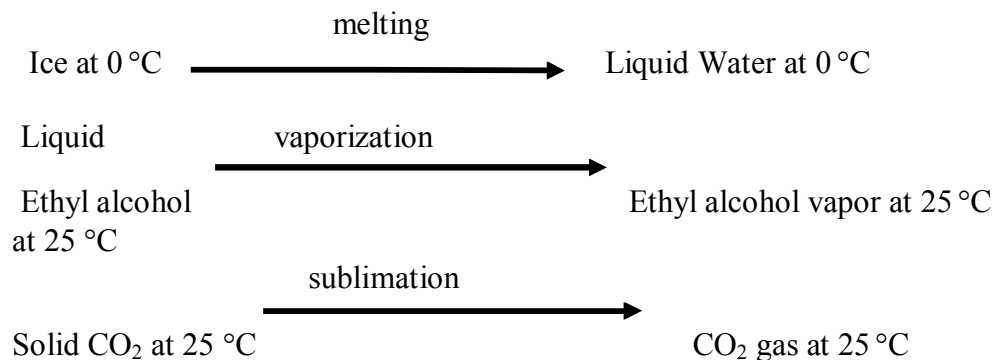


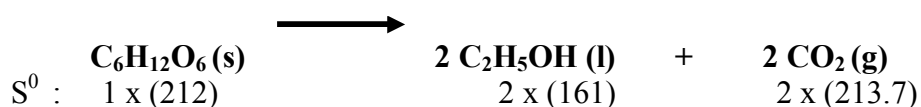
- A reaction in which there is an increase in moles of gas.
This may result from a molecules breaking up, in which case Rule (a) and Rule (b) are related.

Example: the burning of acetylene in oxygen:



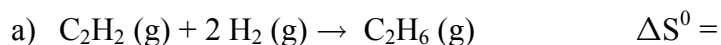
- A process in which a solid changes to a liquid or gas or a liquid changes to a gas



B. ΔS can be calculated if the values of standard entropies are available**Examples:**1. Calculate the change in entropy, ΔS^0 for the fermentation of glucose.The standard entropy of glucose is $C_6H_{12}O_6(s)$ is: 212 J/mol x KThe standard entropy for $C_2H_5OH(l)$ is: 161 J/mol x K
(ethyl alcohol)The standard entropy for $CO_2(g)$ is: 213.7 J/mol x K

$$\Delta S^0 = \Sigma nS^0(\text{products}) - \Sigma nS^0(\text{reactants})$$

$$\Delta S^0 = [(2 \times 161) + 2 \times 213.7] - [1 \times 212] = 537 \text{ J/K}$$

2. Predict the sign of ΔS^0 for each reaction shown below. If you cannot predict the sign for any reaction, state why.3. Using S^0 values in your textbook, calculate ΔS^0 for the synthesis of ammonia.