# ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

# Pre-engineering general chemistry (Chem1011)

## Thermodynamic Equilibrium and Thermochemistry

**Course instructor: Eneyew Tilahun(M.Sc.)**

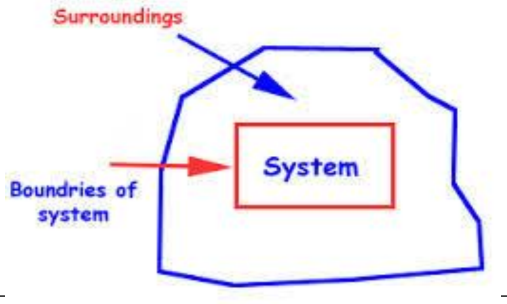
# Principles of thermodynamics

- The word thermodynamics is combination of two words:
  - ✓ thermes meaning heat and dynamics meaning the inherent power to perform.
  - ✓ Thus thermodynamics is concerned with the study of heat, its effect and its properties.
- Branch of science that deals with energy levels and the transfer of energy between systems and between different states of matter”
- Thermodynamics has two parts:-
  - ✓ classical and
  - ✓ statistical

- Classical thermodynamics concerned with macroscopic observables such as P, T, V, $\rho$….
- Statistical thermodynamic deals with microscopic details like dipole moment, molecular size, shape……
- **What are the basic principles of thermodynamics?**
- The four laws of thermodynamics define fundamental physical quantities (temperature, **energy**, and entropy) that characterize thermodynamic systems at thermal equilibrium.

# Thermodynamic terms

- A thermodynamic **system** is the part of the universe which is selected for thermodynamic consideration.
- It is separated from the rest of the universe (environment) called surroundings by a definite boundary.
- So the environment rather than the system is surrounding.
- Example: If you have water in container, the water is your system, the environment outside your container is the surrounding and the wall of the container separating the water from the other environment is boundary.



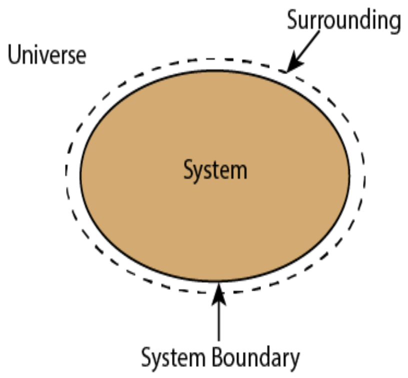
# Class Activity

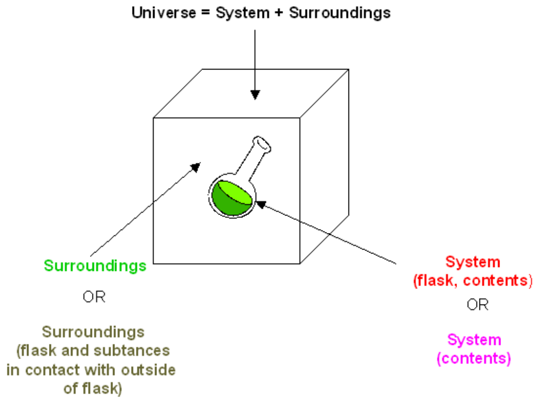
1. Explain the basic Applications of thermodynamics.
2. What is the familiarity of thermodynamics?

## Answer

1. To determine spontaneity of a rxn, in the design of a heating or air conditioning system, used in vehicles, widely used in making of thermal power plants, nuclear plants.
2. It never deal with rate of a reaction within the system.

- The remaining portion of the universe is called surrounding.



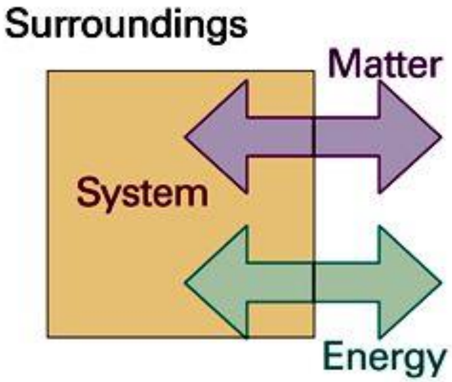


- There are three types of boundary (wall) separating system and surrounding. These are

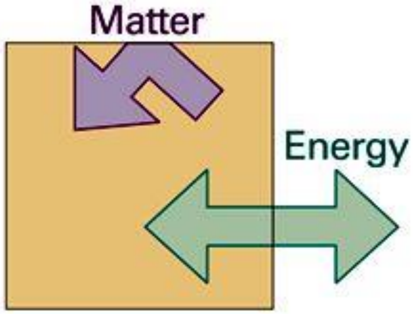
i. A permeable wall: a boundary that allows the passage of both matter and energy.

ii. ii. A diathermal wall: a boundary that prevents the passage of matter and allows the flow of energy.

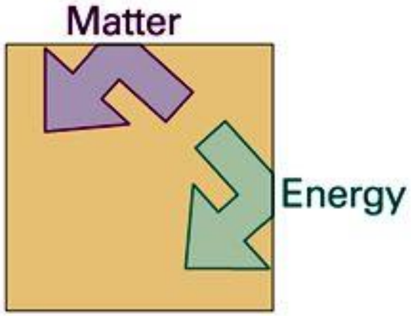
iii. Adiabatic wall: a boundary neither allows the passage of energy nor matter.



(a) Open



(b) Closed



(c) Isolated

## The basic concepts:

**Open system**: Matter and energy can be transferred between system and surrounding.

**Close system**: only energy can be transferred.

**Isolated system**: can exchange neither energy no matter with its surrounding.

# State of a system

- It means a condition of a system described in terms of a certain observable properties, such as T, P V etc. of the system.
- These are known as state variables or thermodynamic variables.
- A system can be expressed by using three of the above variables.
- By specifying two of the three state variables, we can get the other.

# Properties of a system

- It is know that each and every thing can be measured qualitatively or quantitatively.
- In thermodynamics, measurable properties of a system can be divided in to two; they are *extensive* and *intensive* properties.

**A) Extensive Properties**: properties which depend up on the total amount of materials in the system.

**Example**: If you mix 25 mL of water with 10 mL of ethanol, the total volume of the mixture is 35 mL which depend up on their sum. mass,, internal energy, heat contents, free energy, entropy, heat capacity.

**B) Intensive properties (specific property ):** properties which are independent on the amount of material in the system.

**Example**: If you have 1L of water and 10L of water in two containers, what do you think about the boiling point for water in each container?

You know that the boiling point of water is 100°C. Whatever the amount of water, its boiling point is the same in all amount or volume. So boiling point of substance is intensive property.

- Other examples include density, molar properties(molar volume, molar entropy, molar heat capacity, etc.), surface tension, viscosity, specific heat, thermal conductivity, refractive index, P, T, boiling and freezing points, vapor pressure of a liquid.

**NB**:- The ratio of two extensive properties is an intensive property.

## Homogeneous vs heterogeneous properties

- A system is considered to be **homogeneous** if every intensive property has the same value for every point of the system.

- A system is said to be **heterogeneous** if the intensive property of one portion is different from the property of another portion.

**Activity:** Categorize the following as intensive or extensive

| | |
|---|---|
| **a**) Chemical potential | **d**) entropy |
| **b**) Density | **e**) freezing point |
| **c**) Molar heat capacity | **f**) Viscosity |

a. Intensive

b. Intensive

c. Intensive

d. extensive b/c ratio of heat capacity and T (Q is extensive, T is intensive)

e. Intensive

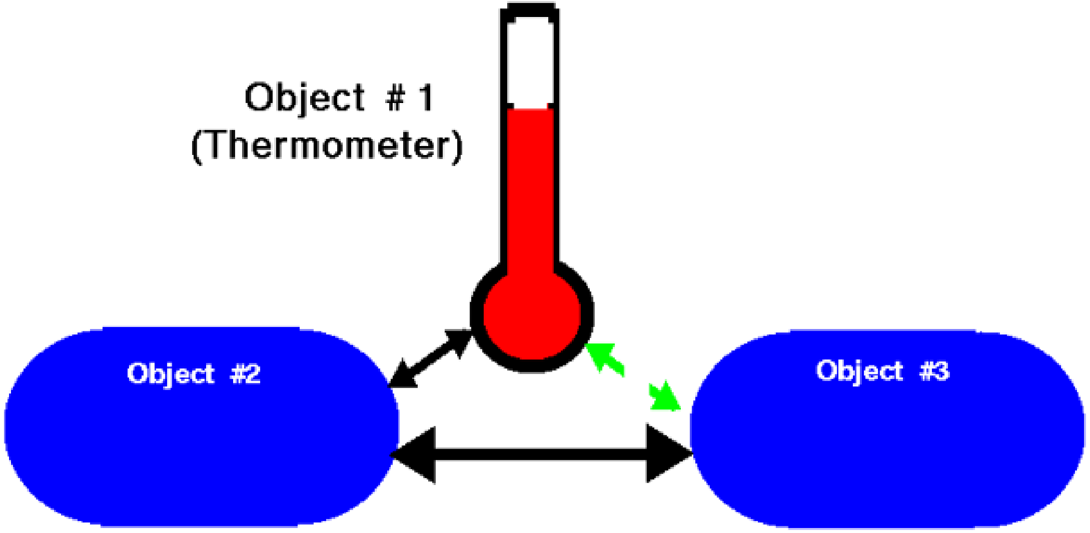
f. Intensive

# Thermodynamic equilibrium, Zero laws of thermodynamics

- A system is in thermodynamic equilibrium if it is in mechanical , thermal and chemical equilibrium.

- **Mechanical equilibrium**: the pressure difference between the system and its surroundings is infinitesimal (pressure is constant).
- **Thermal equilibrium**: is a type of thermodynamic equilibrium in which temperature remains the same in all parts of a system.
- The concept behind thermal equilibrium holds one of the law of thermodynamics which is called **zeroth law of thermodynamics**.

- If system A is in thermal equilibrium with system B and system B is in thermal equilibrium with system C, then a system A is in thermal equilibrium with a system C.



When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.

Objects in thermodynamic equilibrium have the same temperature.

- **Chemical equilibrium:** is a type of thermodynamic equilibrium in which the composition of the system remains constant throughout the system.

# Thermodynamic process

- A process is a change in the state of the system over time, starting with a definite initial state and ending with a definite final state.
- **Process terminology**
- ✓ **Adiabatic – no heat transferred**
- ✓ **Isothermal – constant temperature**
- ✓ **Isobaric – constant pressure**
- ✓ **Isochoric – constant volume**

a) **Adiabatic process**: a process in which there is no exchange of heat between the system and the surrounding ($Q = 0$).

Consider the equation $\Delta U = Q - W$

- When a system expands adiabatically, W is positive (the system does work) so ΔU is negative.
- When a system compresses adiabatically, W is negative (work is done on the system) so ΔU is positive.

b) **Isothermal process**: a process carried out under condition of constant temperature.

- Any heat flow into or out of the system must be slow enough to maintain thermal equilibrium.

**c) Isobaric (Isopiestic) process:** a process that is carried out under condition of constant pressure.

**Example**: Water boiling in a saucepan.

**d)** Isochoric (Isovolumetric) Process: a process in which volume of a system remains constant. When the volume of a system doesn’t change, it will do no work on its surroundings.

$W = 0$ and as a result $\Delta U = Q$

**Exampl**e: Heating gas in a closed container.

**e) Cyclic process**: if a system after undergoing through series of changes in its state come back to initial state. The path followed is known as cyclic Path.

**f) Reversible process**: if at any instant during transformation, the system does not deviate from equilibrium by more than an infinitesimal (very small or values closed to zero but greater than zero) amount.

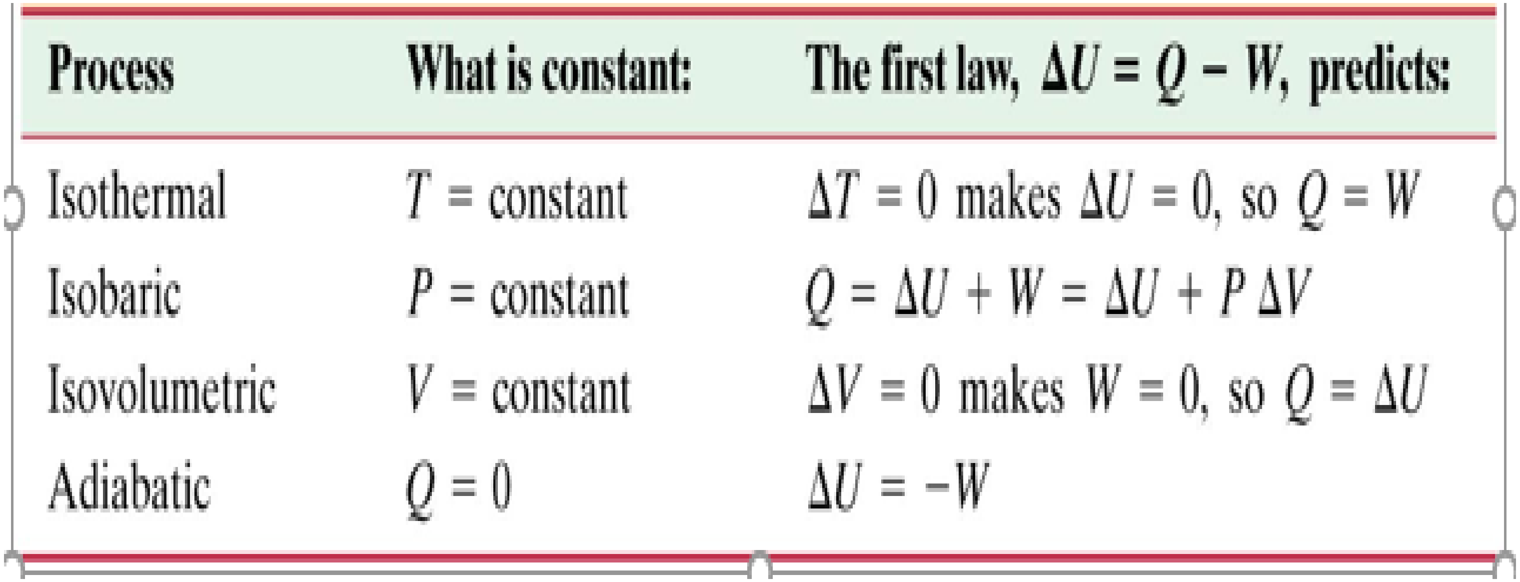
- Change is takes place both forward and backward direction.

**g) Irreversible process**: process that occurs rapidly or spontaneously such that it does not remain in equilibrium during transformation.

**Example:**

# Examples:

- expansion of gas against zero applied pressure,
- dissolution of a solute in solvent, mixing of gases,
- flow of liquid from higher level to lower level.



| Process | What is constant: | The first law, $\Delta U = Q - W$, predicts: |
|---|---|---|
| Isothermal | $T$ = constant | $\Delta T = 0$ makes $\Delta U = 0$, so $Q = W$ |
| Isobaric | $P$ = constant | $Q = \Delta U + W = \Delta U + P\,\Delta V$ |
| Isovolumetric | $V$ = constant | $\Delta V = 0$ makes $W = 0$, so $Q = \Delta U$ |
| Adiabatic | $Q = 0$ | $\Delta U = -W$ |

# State Function

- **State functions** are thermodynamic functions in which change in the values of these quantities do not depend on how change is carried out, but depends on the initial and final state of the system.
- change of a state function during a process depends only on the initial and final states of the system, not on the path of the process.
- Examples: U, S, H, G, chemical potential, $C_V$ and $C_P$
- The finite change of state function $\Delta X$ in a process can be written as X.
- So it can be represented as $\Delta X = \int \Delta X = X_2 - X_1$, where $X_1$ is the value of initial state and $X_2$ is the value of final state of the process respectively.

- **Path function**: is one which depends up on how change in the system takes place. Example heat, q and work, w

$q= \int \text{path}\; dq$ and $w =\int \text{path}\; dw$

The infinitesimals dq and dw are called inexact differentials.

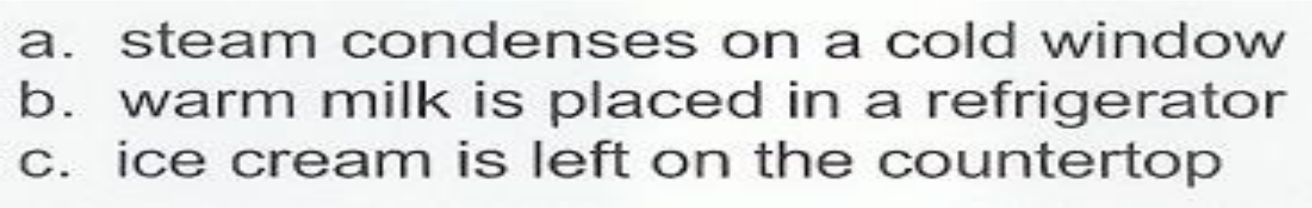
## First Laws of Thermodynamics

## Heat and work

- Heat is a form of energy transfer to or from a system which occurs from hot to cold. Heat gained (absorbed) is considered +; heat lost by system to surroundings is –.

# Activity

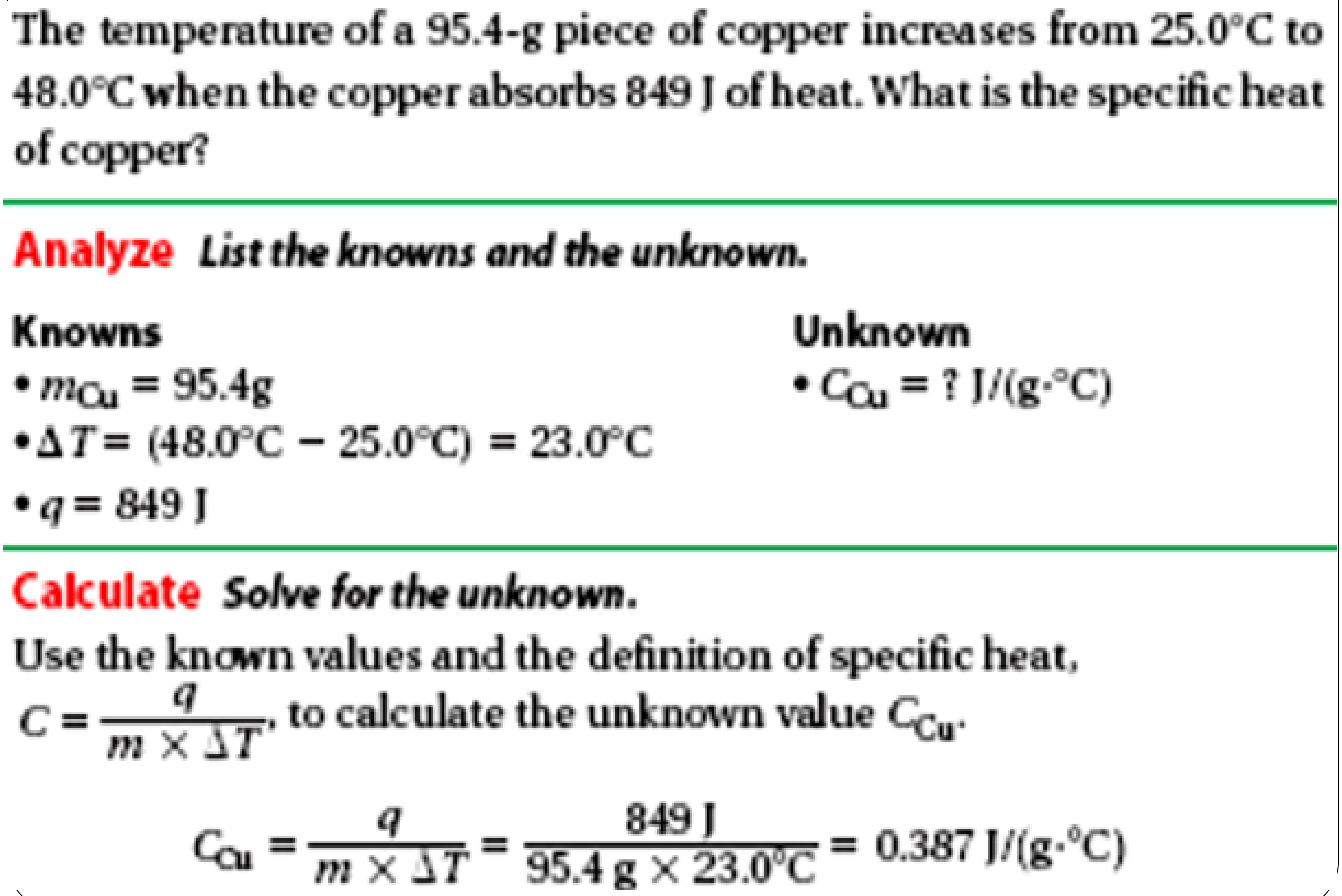
Give the sign of q for each of the following processes when the system and surroundings are at different temperatures.



a. steam condenses on a cold window
b. warm milk is placed in a refrigerator
c. ice cream is left on the countertop

- q = mass (in grams) x $\Delta T$ x C
- $\Delta T$ = change in temperature and C = Specific Heat,
- Units are either: J/(g $^{o}$C) or cal/(g $^{o}$C)

# Examples:



The temperature of a 95.4-g piece of copper increases from 25.0°C to 48.0°C when the copper absorbs 849 J of heat. What is the specific heat of copper?

**Analyze** ***List the knowns and the unknown.***

**Knowns**

- $m_{Cu} = 95.4 g$
- $\Delta T = (48.0°C - 25.0°C) = 23.0°C$
- $q = 849$ J

**Unknown**

- $C_{Cu} = ?$ J/(g·°C)

**Calculate** ***Solve for the unknown.***

Use the known values and the definition of specific heat, $C = \frac{q}{m \times \Delta T}$, to calculate the unknown value $C_{Cu}$.

$$C_{Cu} = \frac{q}{m \times \Delta T} = \frac{849\ J}{95.4\ g \times 23.0°C} = 0.387\ J/(g\cdot°C)$$

# Class work

1. A student must use 225 mL of hot water in a lab procedure. Calculate the amount of heat required to raise the temperature of 225 mL of water from 20℃ to 100℃ (specific heat of water is 4.184 g/J.℃ )
2. Calculate the specific heat capacity of a new alloy if a 15.4 g sample absorbs 393 J when it is heated from 0.0 ℃ to 37.6 ℃

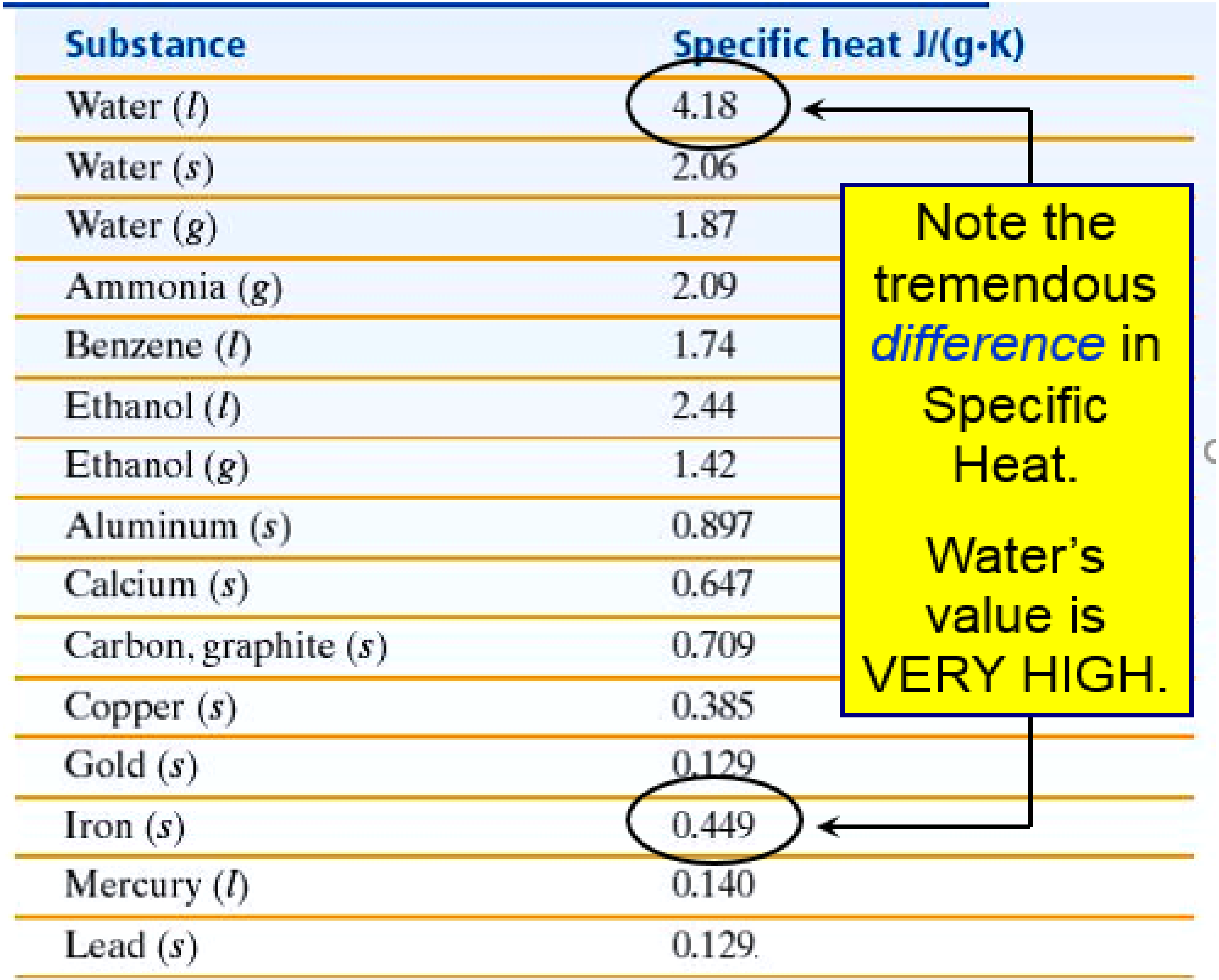
- **Calorimetry** - the measurement of the heat *into* or *out of* a system for chemical and physical processes.
- The device used to *measure* the absorption or release of heat in chemical or physical processes is called a "**Calorimeter**".

- Changes in enthalpy = $\Delta H$ and $q = \Delta H$

- Thus, $q = \Delta H = m \times C \times \Delta T$, where

- H is negative for an exothermic reaction and positive for an endothermic reaction.

# Specific heats of substances at 298.15 K



| Substance | Specific heat J/(g·K) |
|---|---|
| Water (*l*) | 4.18 |
| Water (*s*) | 2.06 |
| Water (*g*) | 1.87 |
| Ammonia (*g*) | 2.09 |
| Benzene (*l*) | 1.74 |
| Ethanol (*l*) | 2.44 |
| Ethanol (*g*) | 1.42 |
| Aluminum (*s*) | 0.897 |
| Calcium (*s*) | 0.647 |
| Carbon, graphite (*s*) | 0.709 |
| Copper (*s*) | 0.385 |
| Gold (*s*) | 0.129 |
| Iron (*s*) | 0.449 |
| Mercury (*l*) | 0.140 |
| Lead (*s*) | 0.129 |

Note the tremendous *difference* in Specific Heat.

Water’s value is VERY HIGH.

- **An exothermic process** is a process that releases energy as heat in to its surroundings.
- **Example**: All combustion reactions are exothermic. Heat is negative in exothermic process.
- **An endothermic process** is a process in which energy is acquired from its surroundings as heat. Heat is positive in this process.
- **Example**: Vaporization of water is endothermic process.

- **The specific heat (s/c)** 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. $C = m \times s$ and $q = m \times s \times \Delta t$

$q = C \times \Delta t$ and $\Delta t = t_{\text{final}} - t_{\text{initial}}$

- ☐ How much heat is given off when an 869 g iron bar cools from 94°C to 5°C? Solution: and $s$ of Fe = 0.444 J/g • °C

$$\Delta t = t_{\text{final}} - t_{\text{initial}} = 5^{o}\text{C} - 94^{o}\text{C} = -89^{o}\text{C},\quad q = ms\Delta t$$

$$= 869\ \text{g} \times 0.444\ \text{J/g} \cdot {}^{o}\text{C} \times -89^{o}\text{C} = -34{,}000\ \text{J}$$

# Work

- Work is the motion against an opposing force
- If an object is displaced through a distance dx against a force f(x), then the amount of work which has to be done is

$$W = -f(x)dx = \int_{x_0}^{x} F\,dx$$

$$w = \int_{x_0}^{x} F\,dx = -(PA)(x - x_0) = -PdV$$

✓ Gravitational work=-mgh

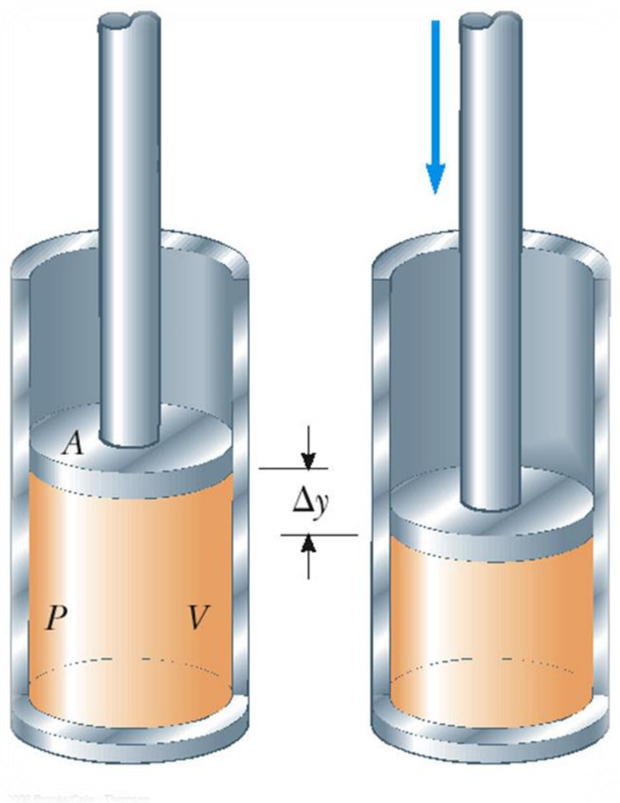
✓ Electrical work = -nFE

✓ Mechanical (pressure-volume work)=-PdV

Example: The capacity to do work is----------------

A) Expansion Work B) Heat C) Energy D) All

- Work don the gas:



$$W = -P\Delta V$$

B/c work is done by the gas

# Activity

**1**. A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands (a) against a vacuum and (b) against a constant pressure of 3.7 atm? **Solution** $w = -P\,\Delta V$

(a) $\Delta V = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $P = 0\text{ atm}$

$$W = -0\text{ atm} \times 3.8\text{ L} = 0\text{ L.atm} = 0\text{ joules}$$

(b) $\Delta V = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $P = 3.7\text{ atm}$

$$w = -3.7\text{ atm} \times 3.8\text{ L} = -14.1\text{ L•atm}$$

$$w = -14.1\ \cancel{\text{L•atm}} \times \frac{101.3\text{ J}}{1\cancel{\text{L•atm}}} = -1430\text{ J}$$

- Consider the equation: $w = -Mgh$
- Negative sign is in accord with convention that work done by a system is taken to be a negative quantity.
- If we divide Mg by A, the area of the piston, and multiply by h

$$w = -\frac{Mg}{A} \cdot Ah$$

- But Mg/A is the external pressure exerted on the gas and Ah is the change in volume experienced by the gas:

$$w = -P_{\text{ext}} \Delta V$$

Note that $\Delta V > 0$ in an expansion, so $w < 0$. Clearly, the external pressure must be less than the pressure of the inital state of the gas in order that the expansion occur. After the expansion, $P_{\text{ext}} = P_{\text{f}}$.

- After compression, $P_{ext} = P_f$, work is positive because work is done on the (gas) system when it is compressed.
- If $P_{ext}$ is not constant during the expansion, the work is given by

$$w = -\int_{V_i}^{V_f} P_{ext}\, dV$$

Consider an ideal gas that occupies 1.00 $dm^3$ at a pressure of 2.00 bar. If the gas is compressed isothermally at a constant external pressure, $P_{ext}$, so that the final volume is 0.500 $dm^3$, what is the smallest value $P_{ext}$ can have? Calculate the work involved using this value of $P_{ext}$.

SOLUTION: For a compression to occur, the value of $P_{\text{ext}}$ must be at least as large as the final pressure of the gas. Given the inital pressure and volume, and the final volume, we can determine the final pressure. The final pressure of the gas is

$$P_{\text{f}} = \frac{P_{\text{i}} V_{\text{i}}}{V_{\text{f}}} = \frac{(2.00\ \text{bar})(1.00\ \text{dm}^3)}{0.500\ \text{dm}^3} = 4.00\ \text{bar}$$

This is the smallest value $P_{\text{ext}}$ can be to compress the gas isothermally from 1.00 $\text{dm}^3$ to 0.500 $\text{dm}^3$. The work involved using this value of $P_{\text{ext}}$ is

$$w = -P_{\text{ext}}\,\Delta V = -(4.00\ \text{bar})(-0.500\ \text{dm}^3) = 2.00\ \text{dm}^3\cdot\text{bar}$$

$$= (2.00\ \text{dm}^3\cdot\text{bar})(10^{-3}\ \text{m}^3\cdot\text{dm}^{-3})(10^5\ \text{Pa}\cdot\text{bar}^{-1}) = 200\ \text{Pa}\cdot\text{m}^3 = 200\ \text{J}$$

- Calculate the work done when 50 g of iron reacts with hydrochloric acid in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C.

***Answer*** In (a) the volume cannot change, so no expansion work is done and $w = 0$. In (b) the gas drives back the atmosphere and therefore $w = -p_{ex}\Delta V$. We can neglect the initial volume because the final volume (after the production of gas) is so much larger and $\Delta V = V_f - V_i \approx V_f = nRT/p_{ex}$, where $n$ is the amount of $H_2$ produced. Therefore,

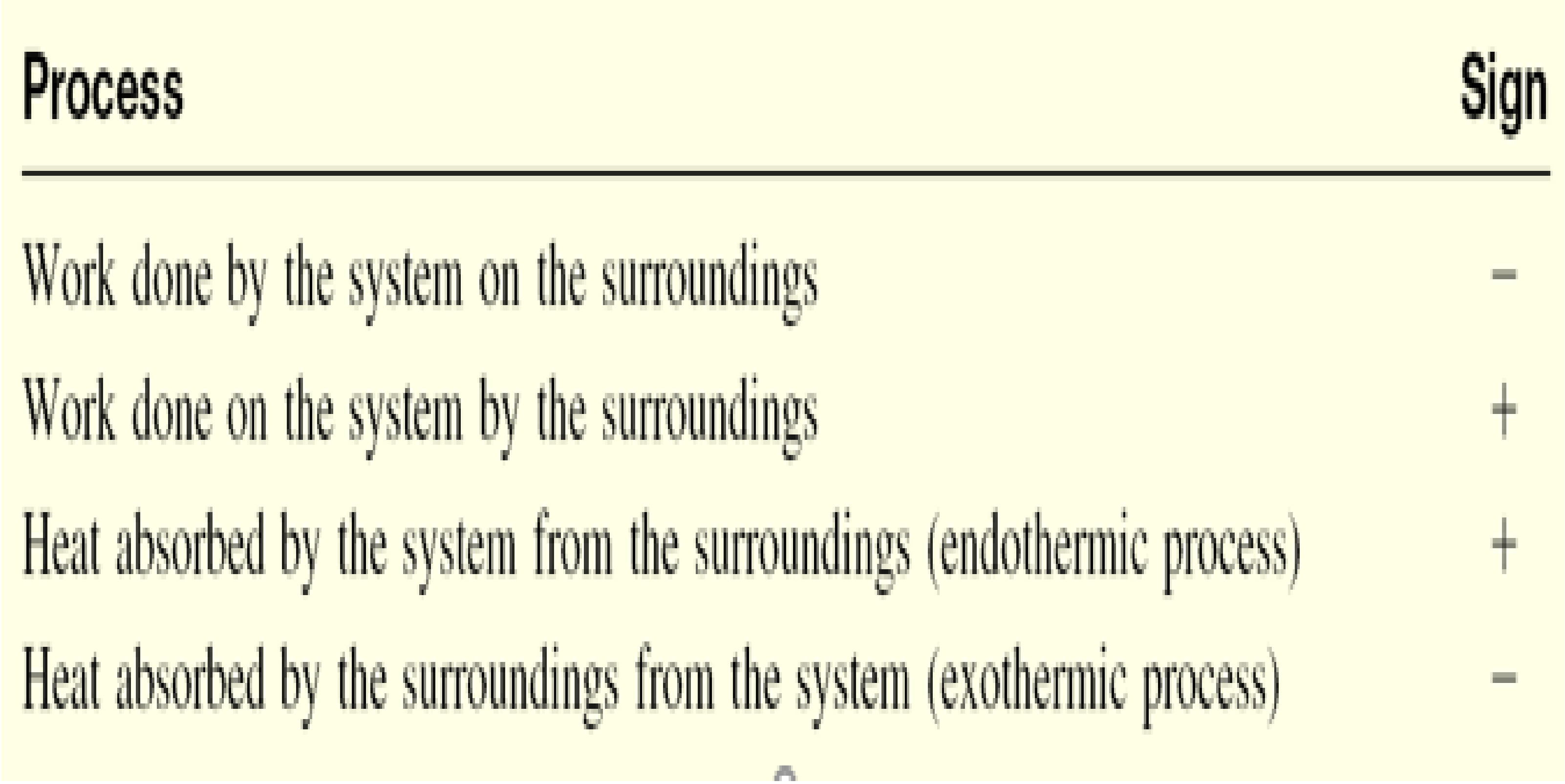
$$w = -p_{ex}\Delta V \approx -p_{ex} \times \frac{nRT}{p_{ex}} = -nRT$$

Because the reaction is $Fe(s) + 2\,HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$, we know that 1 mol $H_2$ is generated when 1 mol Fe is consumed, and $n$ can be taken as the amount of Fe atoms that react. Because the molar mass of Fe is 55.85 g mol$^{-1}$, it follows that

$$w \approx -\frac{50\ \text{g}}{55.85\ \text{g mol}^{-1}} \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})$$

$$\approx -2.2\ \text{kJ}$$

# Summery



| 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) | − |

- The first law of thermodynamics is known as the law of conservation of energy.
- It states that energy can be neither created nor destroyed.
- Mathematical formulation in terms of change of internal energy, heat and work for first law is: $\Delta U = q + w$.
- Assume that $U_1$ and $U_2$ is the initial and final value of internal energy after w is done on the system and heat,

Final energy = initial energy + heat absorbed + work done on the system

$$U_2 = U_1 + q + W$$

$$U_2 - U_1 = +q + W$$

Since $U_2 - U_1 = \Delta U$

$$\Delta U = q + W$$

- If **no work is done, W**=0, the above equation become , $\Delta U = q$
- For **adiabatic process (no exchange of heat), q=0,** the above equation become

$$\Delta U = W$$

- If there is no change in internal energy of the system, $\Delta U$ the first law may be written as $q = -W$.
- Thus, when the energy of the system is kept constant then heat absorbed by the system is equal to the work done by the system $W = -q$.
- Thus, the energy of the system kept constant and work is done on the system, then heat must flow from the system to the surroundings.

Example: If an electric motor produces 15 KJ of energy each second as mechanical work and lost 2 KJ as heat to the surrounding, what is the change in internal energy?

ΔU = -2 K J-15 KJ = -17 KJ.

-15 indicate that the energy (the capacity to do work) is produced by the electric motor; mean work is done by the motor.

2) Suppose that, when the spring was wound, 100KJ of work was done on it. But 15KJ escaped to the surroundings as heat. What is the change in internal energy of the spring?

$$\Delta U = +100KJ - 15KJ = +85KJ$$

# Thermochemistry

- **Is chemistry of reaction of heat.**
- Thermochemistry is the branch of physical chemistry deals with the heat change during chemical or physical process.
- Thermochemistry is the study of heat change in chemical reactions.
- Since heat is depends on the path of the reaction, it is more convenient to express the energy of the system in terms of thermodynamic quantities as they are independent of path.
- The energy changes in chemical reactions are due to bond breaking and formation of new bonds.

# Internal energy and enthalpy of reaction

- **Enthalpy of reaction**: is the amount of heat absorbed or evolved in the transformation of reactant at a given temperature and pressure in to products at the same temperature and pressure.
- **Example**: $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H = -285.3KJ \; at \; 298 \; K \; and \; 1 \; atm$

## Conditions at which enthalpy of a reaction depends on

- ✓ **Constant volume**: when the reaction carried in closed and rigid container. The first law of thermodynamics becomes:- $\boldsymbol{\Delta U = q_v}$

$$\Delta U = \sum U_{product} - \sum U_{reactant} \qquad (*)$$

- ✓ **At constant pressure:** the system is either kept open to the atmosphere or confined within the vessel in which a constant external pressure is exerted. If w is pressure-volume work only, from the first law of thermodynamics,

$q_p = \Delta U + W = \Delta U + P\Delta V$ from equation (*), the above equation becomes $q_p = \left(\sum U_P - \sum U_R\right) + P(V_P - V_R)$

- Collect like terms (p with p and R with R), the equation becomes:

$$q_p = \left(\sum U_P + PV_P\right) - \left(\sum U_R + PV_R\right)$$

Since H =U+PV, the equation above is becomes: $q_p = \sum H_P - \sum H_R$

- The difference in the enthalpy of the product and the reactant is the change in enthalpy of the system. $q_p = \Delta H$ but $\Delta H = \Delta U + P\Delta V$
- For the system involving liquid and solid the volume of reactant equal to the volume of product, so $\Delta H = \Delta U$
- For an ideal gas, PV = nRT, then $\Delta H = \Delta U + [nRT]_{product} - [nRT]_{reactant}$

take constants as common from both sides of the equation & becom

$$\Delta H = \Delta U + RT(n_p - n_R)$$

$$\Delta H = \Delta U + \Delta nRT \; \ldots\ldots\ldots..$$

$$q_p = q_V + \Delta nRT$$

## Class work

1) For conversion of a mole of $SO_{2(g)}$ in to $SO_{3(g)}$ the internal energy of reaction at constant volume at 298K is -97.027KJ. Calculate the enthalpy of a reaction at constant pressure. The reaction is

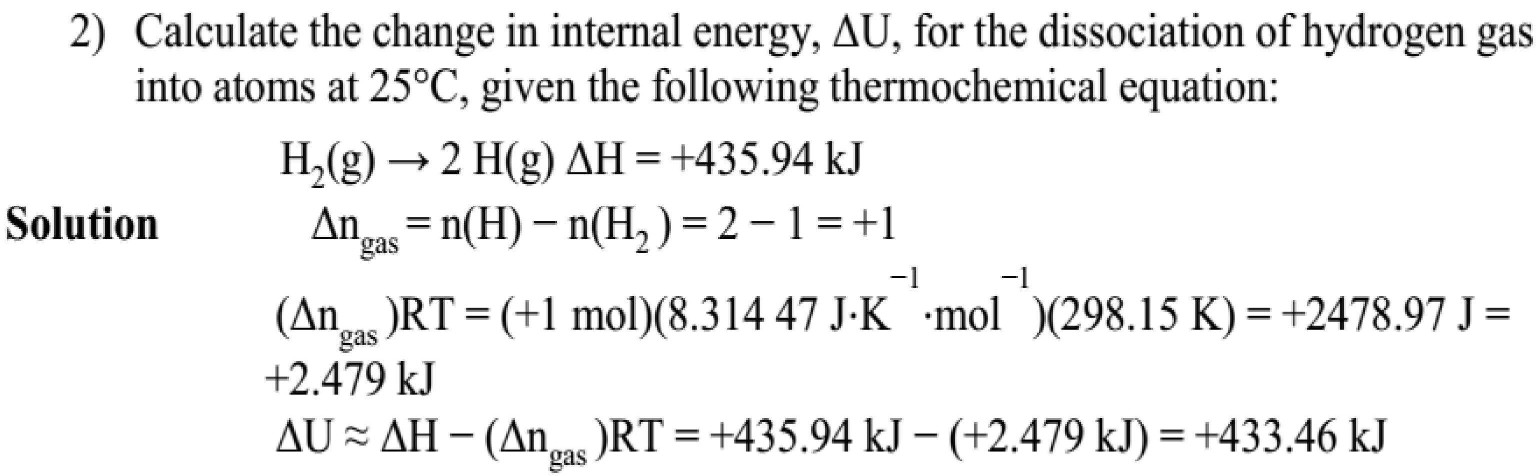
$$SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow SO_{3(g)}$$

Solution

From the above $\Delta n = n_p - n_r = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$

$$\Delta H = \Delta U + \Delta nRT = (-97.02kJmol^{-1})\left(-\frac{1}{2}\right)(RT)$$

$$\Delta H = -98.267KJmol^{-1}$$



2) Calculate the change in internal energy, ΔU, for the dissociation of hydrogen gas into atoms at 25°C, given the following thermochemical equation:

$$H_2(g) \rightarrow 2\,H(g)\quad \Delta H = +435.94\ \text{kJ}$$

**Solution**

$$\Delta n_{gas} = n(H) - n(H_2) = 2 - 1 = +1$$

$$(\Delta n_{gas})RT = (+1\ \text{mol})(8.314\,47\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298.15\ \text{K}) = +2478.97\ \text{J} = +2.479\ \text{kJ}$$

$$\Delta U \approx \Delta H - (\Delta n_{gas})RT = +435.94\ \text{kJ} - (+2.479\ \text{kJ}) = +433.46\ \text{kJ}$$

## Activity

3. How much heat is evolved when 266 g of white phosphorus ($P_4$) burn in air? (Mwt = 124 g/mol)

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

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

$$\boxed{\text{i.e heat energy evolved} = \frac{\text{mass of asubstance}}{\text{molar mass of a substance}} \text{x}\Delta H}$$

# Laws of Thermochemistry

1) **Lavoisier or Laplace law**: the quantity of heat required for the decomposition of a compound in to its elements must be equal to the heat evolved during the formation of a compound from its element.

   In this time thermochemical equations can be reversed and the sign of $\Delta H^{\circ}$ is changed.

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_2 \rightarrow HCl_{(g)} \quad \Delta H^{\circ} = -92.31KJ$$

   May be written as

$$HCl_{(g)} \rightarrow \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_2 \qquad \Delta H^{\circ} = +92.31KJ$$

2) **Hess's Law**: states that standard enthalpy of overall reaction is the sum of the standard enthalpies of the individual reactions in to which a reaction may be divided.

Example:

1) Consider formation of an aqueous solution of ammonium chloride from gaseous hydrochloric acid and ammonia.

Case1;

$$HCl_{(g)} + NH_{3(g)} \rightarrow NH_4Cl_{(s)} \qquad \Delta H^\circ = -177.80KJ$$

$$NH_4Cl_{(s)} + aq \rightarrow NH_4Cl_{(aq)} \qquad \Delta H^\circ = +16.32KJ$$

Their sum

$$HCl_{(g)} + NH_{3(g)} + aq \rightarrow NH_4Cl_{(aq)} \qquad \Delta H^\circ = -161.48KJ$$

Case2:

$$HCl_{(g)} + aq \rightarrow HCl_{(aq)} \qquad \Delta H^\circ = -74.91KJ$$

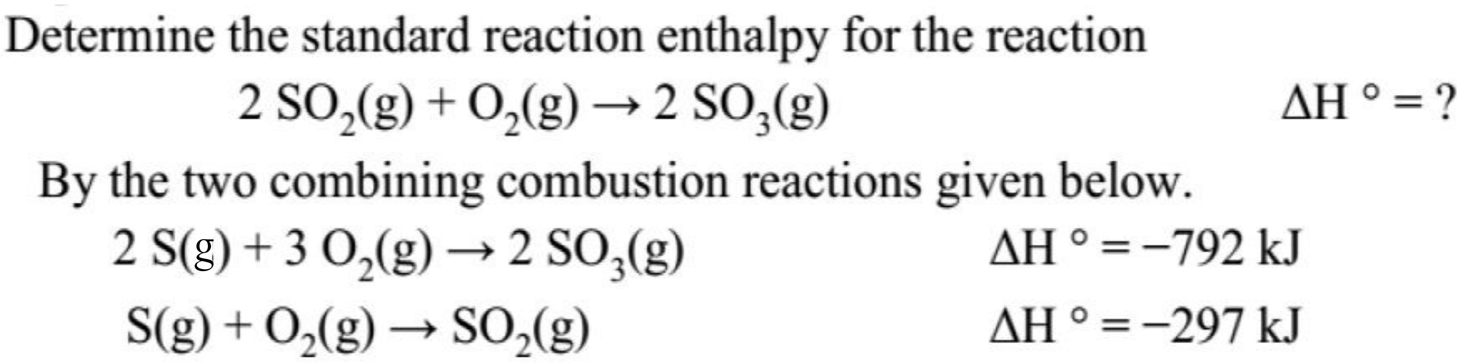
$$NH_{3(g)} + aq \rightarrow NH_{3(aq)} \qquad \Delta H^\circ = -35.15KJ$$

$$HCl_{(aq)} + NH_{3(aq)} \rightarrow NH_4Cl_{(aq)} \qquad \Delta H^\circ = -51.42KJ$$

- Adding the above reactions together gives:

$$HCl_{(g)} + NH_{3(g)} + aq \rightarrow NH_4Cl_{(aq)} \qquad \Delta H^{\circ} = -161.48KJ$$

## Class Activity



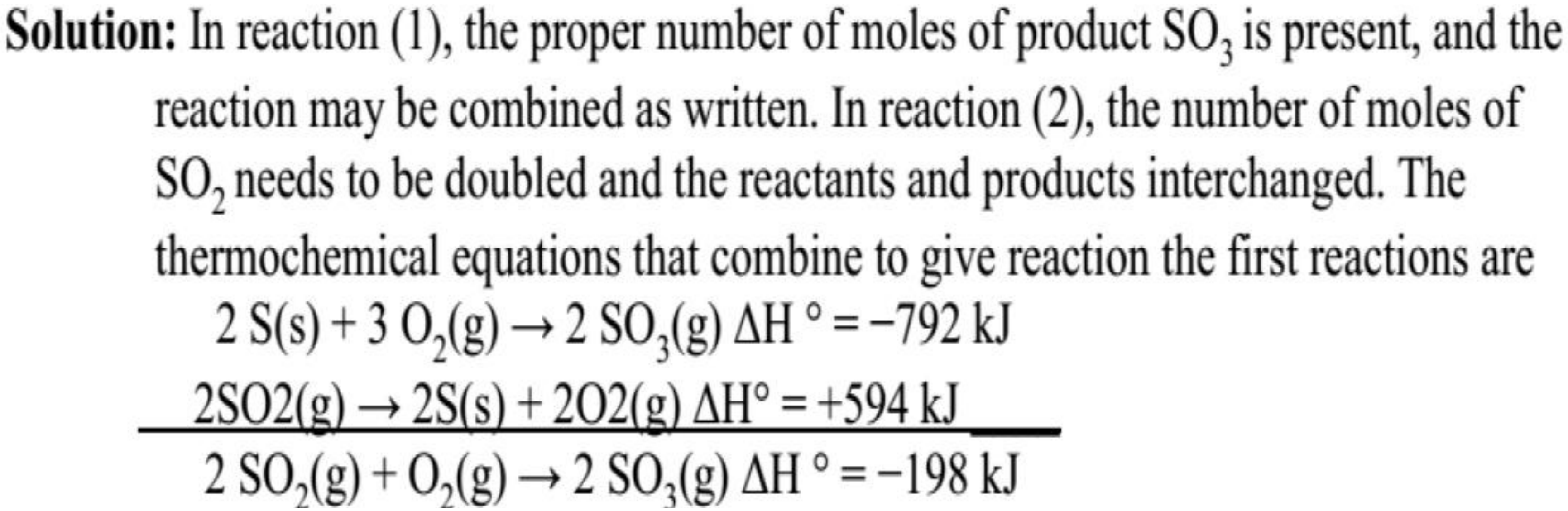
Determine the standard reaction enthalpy for the reaction

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g) \qquad \Delta H^{\circ} = ?$$

By the two combining combustion reactions given below.

$$2\ S(g) + 3\ O_2(g) \rightarrow 2\ SO_3(g) \qquad \Delta H^{\circ} = -792\ kJ$$

$$S(g) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H^{\circ} = -297\ kJ$$



**Solution:** In reaction (1), the proper number of moles of product $SO_3$ is present, and the reaction may be combined as written. In reaction (2), the number of moles of $SO_2$ needs to be doubled and the reactants and products interchanged. The thermochemical equations that combine to give reaction the first reactions are

$$2\ S(s) + 3\ O_2(g) \rightarrow 2\ SO_3(g)\ \Delta H^{\circ} = -792\ kJ$$

$$\underline{2SO2(g) \rightarrow 2S(s) + 2O2(g)\ \Delta H^{\circ} = +594\ kJ}$$

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)\ \Delta H^{\circ} = -198\ kJ$$

# Class Activity

**1**. $C + O_2 \rightarrow CO_{2,}$ find $\Delta H°$

$C + ½O_2 \rightarrow CO$ $\Delta H° = – 110.5$ kJ

$CO + ½O_2 \rightarrow CO_2$ $\Delta H° = – 283.0$ kJ

$C + CO + O_2 \rightarrow CO + CO_2$ s$\Delta H° = – 393.5$ kJ

I.e. $C+ O_2 \rightarrow CO_2$ $\Delta H° =$ **– 393.5 kJ**

# Homework

Consider the reaction given below in the formation of $CO_2$ and water as shown:

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

$$C_3H_8\,(g) \longrightarrow 3\,C + 4\,H_2\,(g)$$

$$3\,C + 3\,O_2\,(g) \longrightarrow 3\,CO_2\,(g)$$

$$4\,H_2\,(g) + 2\,O_2\,(g) \longrightarrow 4\,H_2O\,(l)$$

Use the standard enthalpy of formation for each species, calculate change of enthalpy.

# Second Laws of Thermodynamics

- The first law is not capable of predicting the direction of a process.
- So the second law was developed for prediction of the direction of the process (reaction).

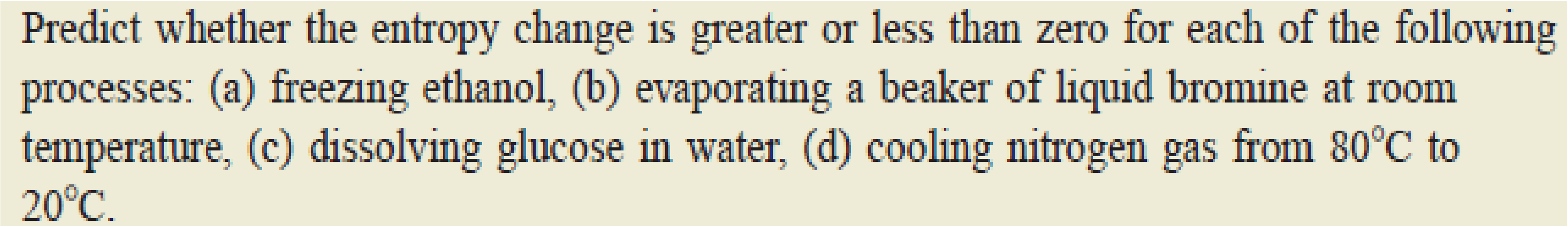
## statements of the 2nd law

- ✓ Entropy increases in irreversible process.
- ✓ Heat cannot pass from a colder body to a warmer body.

Entropy

- ✓ Measure of the randomness or disorderness in a molecular system. $S_{gas} > S_{liqid} > S_{solid}$ and given as: $dS = \frac{dQ_{rev}}{T}$

# Activity



Predict whether the entropy change is greater or less than zero for each of the following processes: (a) freezing ethanol, (b) evaporating a beaker of liquid bromine at room temperature, (c) dissolving glucose in water, (d) cooling nitrogen gas from 80°C to 20°C.

a. **$\Delta S<0$, more ordered**

b. **$\Delta S>0$, less ordered**

c. **$\Delta S>0$, order decrease**

d. **$\Delta S<0$, as temperature decrease, $\Delta S$ decrease**

# Enthalpy and entropy relation

$$H = U + PV$$

$$or$$

$$\Delta H = d(U + PV) = dU + dPV + PdV$$

But $TdS = dU + PdV$ so the above equation becomes: $\Delta H = TdS + VdP$

- ❑ Entropy of universe $\Delta S_{(universe)} = \Delta S_{(system)} + \Delta S_{surroundings}$
- ❑ Since $dS = \frac{dQ_{rev}}{T}$ then $\Delta S_{surroundings} = \frac{-q_{system}}{T} = \frac{q_{surrounding}}{T}$

- ➢ **For reversible isolated process the change of entropy is Zero.**
- ➢ **For irreversible isolated process the entropy change is greater than zero.**
- ➢ **Entropy change for isothermal reversible process($\Delta U = O\ because\ dT = 0$)**

$$\Delta \boldsymbol{S}_{sys} = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right) = -nR\ln\left(\frac{P_2}{P_1}\right)$$

- Mathematically second law of thermodynamics described as:

For a spontaneous process: $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

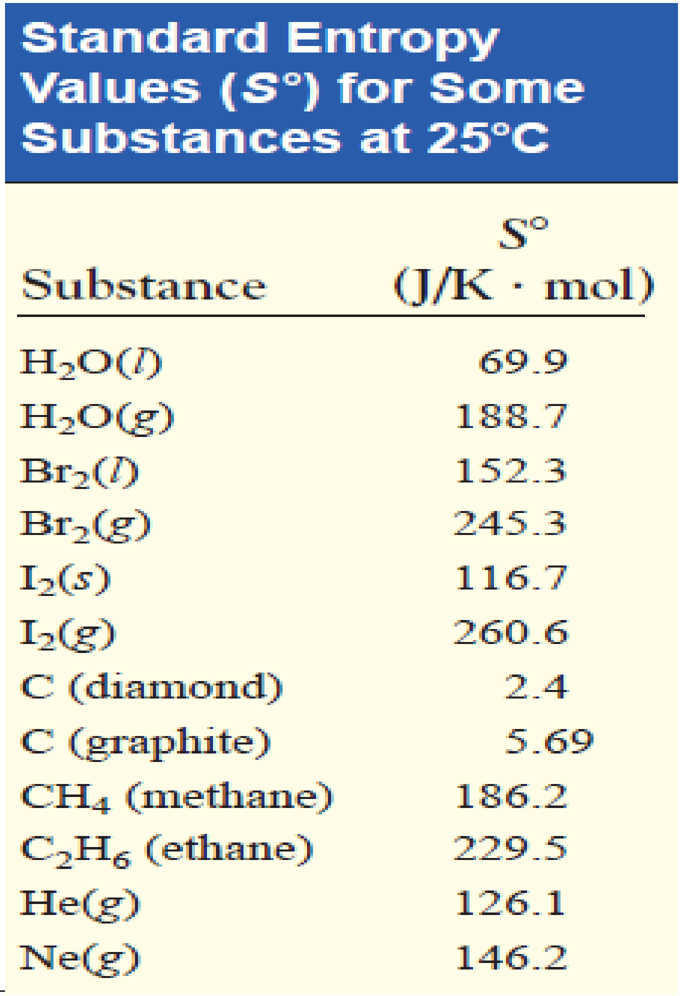
For an equilibrium process: $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

- Consider the chemical reaction given below:

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

$$\Delta S^\circ_{\text{rxn}} = [cS^\circ(\text{C}) + dS^\circ(\text{D})] - [aS^\circ(\text{A}) + bS^\circ(\text{B})]$$

$$\Delta S^\circ_{\text{rxn}} = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants})$$

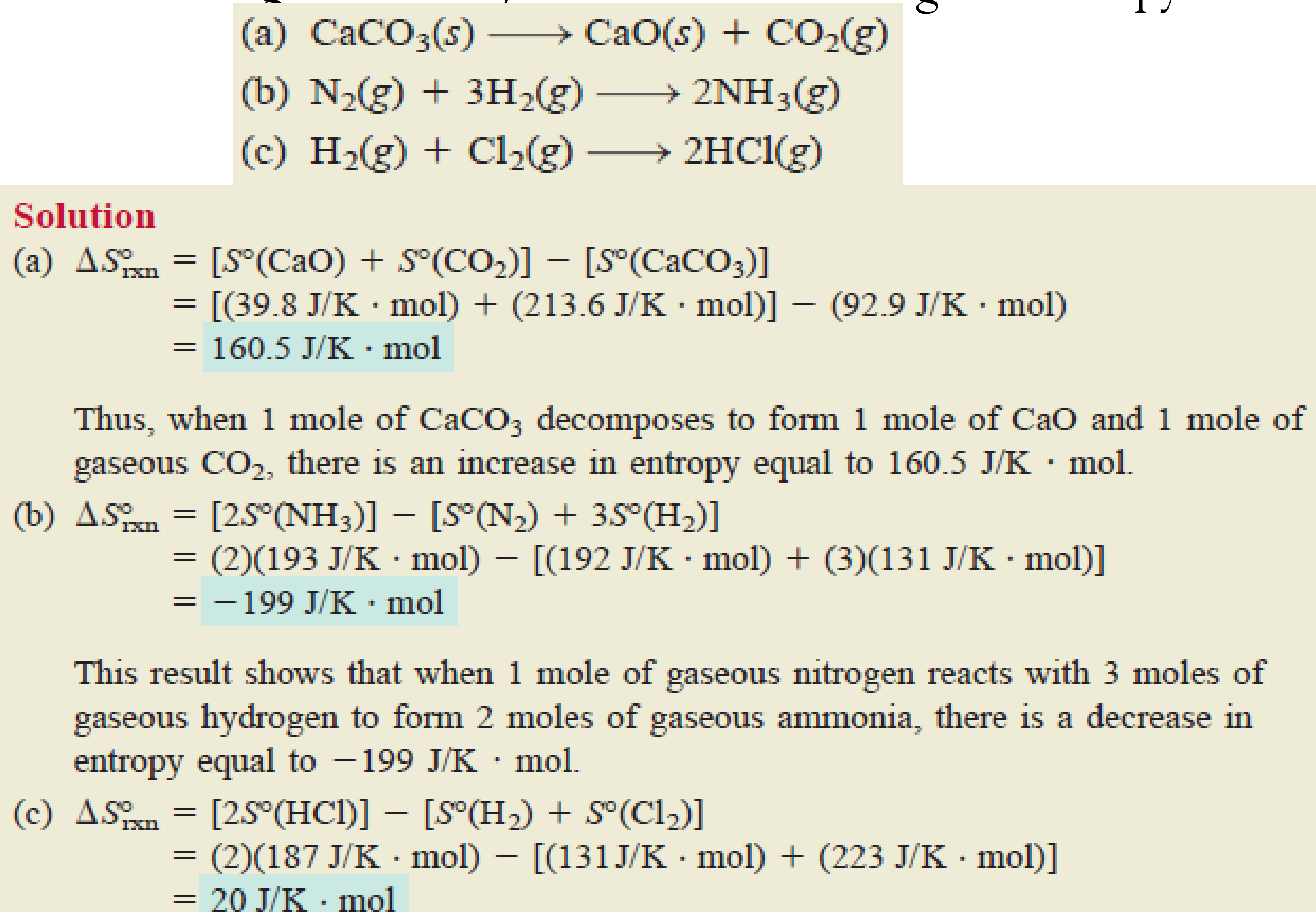


**Standard Entropy Values ($S°$) for Some Substances at 25°C**

| Substance | $S°$ (J/K · mol) |
|---|---|
| $H_2O(l)$ | 69.9 |
| $H_2O(g)$ | 188.7 |
| $Br_2(l)$ | 152.3 |
| $Br_2(g)$ | 245.3 |
| $I_2(s)$ | 116.7 |
| $I_2(g)$ | 260.6 |
| C (diamond) | 2.4 |
| C (graphite) | 5.69 |
| $CH_4$ (methane) | 186.2 |
| $C_2H_6$ (ethane) | 229.5 |
| $He(g)$ | 126.1 |
| $Ne(g)$ | 146.2 |

# Class Activity

For the reaction given below, determine the change in entropy.



(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

(b) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(c) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

**Solution**

(a)
$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= [S^\circ(\text{CaO}) + S^\circ(\text{CO}_2)] - [S^\circ(\text{CaCO}_3)]\\ &= [(39.8\ \text{J/K}\cdot\text{mol}) + (213.6\ \text{J/K}\cdot\text{mol})] - (92.9\ \text{J/K}\cdot\text{mol})\\ &= 160.5\ \text{J/K}\cdot\text{mol}\end{aligned}$$

Thus, when 1 mole of $CaCO_3$ decomposes to form 1 mole of CaO and 1 mole of gaseous $CO_2$, there is an increase in entropy equal to 160.5 J/K · mol.

(b)
$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= [2S^\circ(\text{NH}_3)] - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)]\\ &= (2)(193\ \text{J/K}\cdot\text{mol}) - [(192\ \text{J/K}\cdot\text{mol}) + (3)(131\ \text{J/K}\cdot\text{mol})]\\ &= -199\ \text{J/K}\cdot\text{mol}\end{aligned}$$

This result shows that when 1 mole of gaseous nitrogen reacts with 3 moles of gaseous hydrogen to form 2 moles of gaseous ammonia, there is a decrease in entropy equal to −199 J/K · mol.

(c)
$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= [2S^\circ(\text{HCl})] - [S^\circ(\text{H}_2) + S^\circ(\text{Cl}_2)]\\ &= (2)(187\ \text{J/K}\cdot\text{mol}) - [(131\ \text{J/K}\cdot\text{mol}) + (223\ \text{J/K}\cdot\text{mol})]\\ &= 20\ \text{J/K}\cdot\text{mol}\end{aligned}$$

# Homework

1. Two gaseous pollutants that form in auto exhaust are CO and NO. An environmental chemist is studying ways to convert them to less harmful gases through the following equation:

$$CO(g) + NO(g) \longrightarrow CO_2(g) + \tfrac{1}{2}N_2(g) \quad \Delta H = ?$$

Given the following information, calculate the unknown $\Delta H$:

$$\text{Equation A:} \quad CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H_A = -283.0\,\text{kJ}$$

$$\text{Equation B:} \quad N_2(g) + O_2(g) \longrightarrow 2NO(g) \quad \Delta H_B = 180.6\,\text{kJ}$$

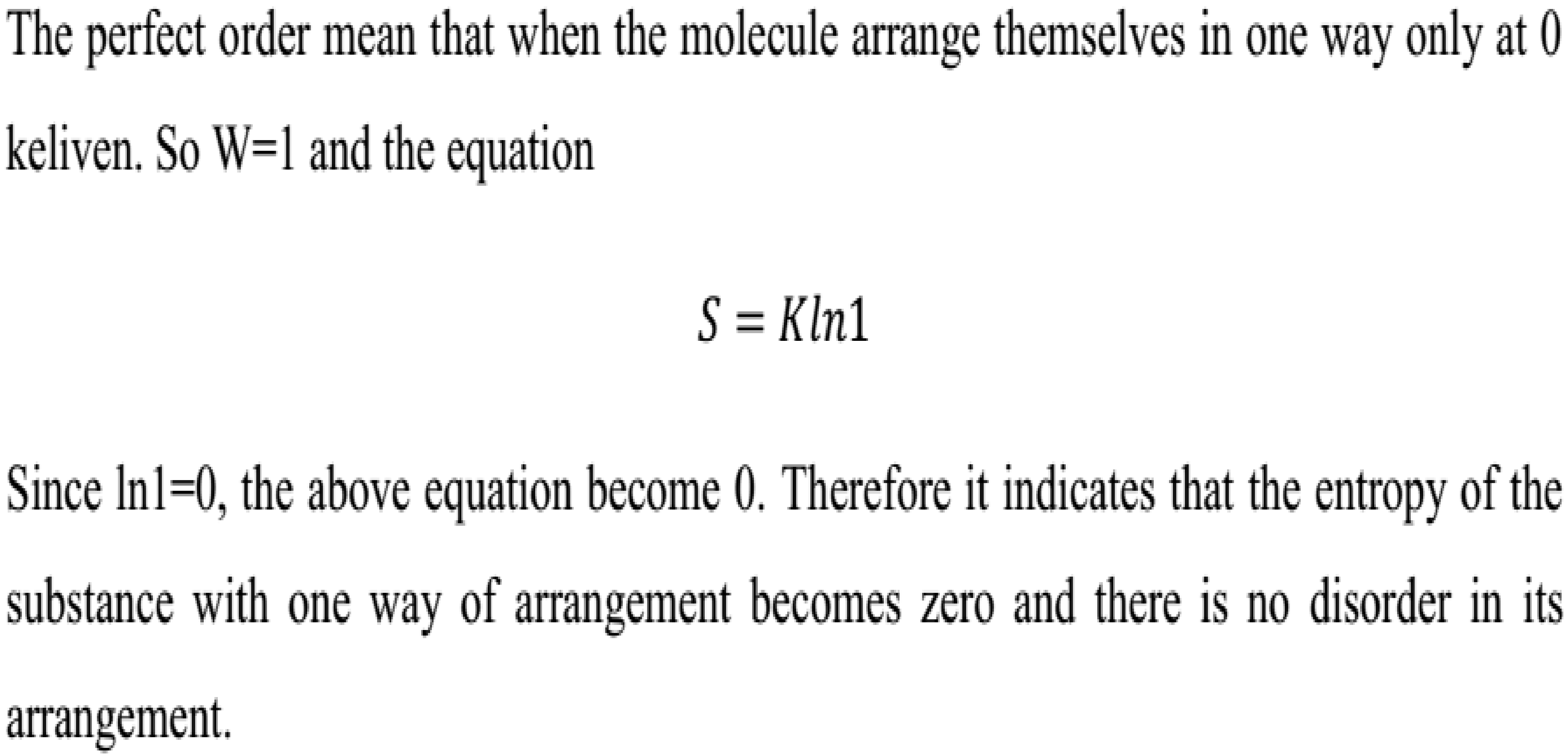
# Third Law of Thermodynamics

- The entropy of all the perfect crystalline solids is zeros at absolute zero temperature.
- The third law of thermodynamics is also referred to as Nernst law. It provides the basis for the calculation of absolute entropies of the substances, $\lim_{T \to 0} \Delta S = 0$

- ✓ It explains the behavior of solids at very low temperature.
- ✓ It helps in analyzing chemical and phase equilibrium.

- Entropy and molecular arrangement is given by Boltzmann equation: $S = K\ln W$ where $K = \frac{R}{N_A} = 1.38 \times 10^{-23} JK^{-1}$

W is the number of ways of molecular arrangements/microstates.



The perfect order mean that when the molecule arrange themselves in one way only at 0 keliven. So W=1 and the equation

$$S = K\ln 1$$

Since ln1=0, the above equation become 0. Therefore it indicates that the entropy of the substance with one way of arrangement becomes zero and there is no disorder in its arrangement.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surround}$$

$$\Delta S_{surr} = \frac{-\Delta H^\circ_{sys}}{T}$$

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H^\circ_{sys}}{T}$$

$$\underbrace{T\Delta S_{universe}} = T\Delta S_{system} + -\Delta H^\circ_{sys}$$

**= – Gibbs Free Energy**

$$\underbrace{T\Delta S_{universe}} = T\Delta S_{system} + -\Delta H^{\circ}_{sys}$$

**= – Gibbs Free Energy**

Make this equation nicer:

$$-T\Delta S_{universe} = \Delta H^{\circ}_{sys} - T\Delta S_{system}$$

$$\boxed{\Delta G = \Delta H^{\circ}_{sys} - T\Delta S_{system}}$$

$$\Delta G^\circ_{\text{rxn}} = \Sigma n\Delta G^\circ_{\text{f}}(\text{products}) - \Sigma m\Delta G^\circ_{\text{f}}(\text{reactants})$$

Calculate the standard free-energy changes for the following reactions at 25°C.

(a) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

(b) $2MgO(s) \longrightarrow 2Mg(s) + O_2(g)$

# solution

$$\Delta G^\circ_{\text{rxn}} = [\Delta G^\circ_{\text{f}}(CO_2) + 2\Delta G^\circ_{\text{f}}(H_2O)] - [\Delta G^\circ_{\text{f}}(CH_4) + 2\Delta G^\circ_{\text{f}}(O_2)]$$

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [(-394.4\ \text{kJ/mol}) + (2)(-237.2\ \text{kJ/mol})] - \\ &\qquad [(-50.8\ \text{kJ/mol}) + (2)(0\ \text{kJ/mol})] \\ &= -818.0\ \text{kJ/mol}\end{aligned}$$

$$\Delta G^\circ_{\text{rxn}} = [2\Delta G^\circ_{\text{f}}(Mg) + \Delta G^\circ_{\text{f}}(O_2)] - [2\Delta G^\circ_{\text{f}}(MgO)]$$

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [(2)(0\ \text{kJ/mol}) + (0\ \text{kJ/mol})] - [(2)(-569.6\ \text{kJ/mol})] \\ &= 1139\ \text{kJ/mol}\end{aligned}$$

# Exercise on thermodynamics

1. What is the heat required to convert 25 grams of ice at -10 °C into steam at 150 °C?
2. What quantity of heat is necessary to convert 50 g of ice at 0 degrees C into steam at 100 degrees C?
3. How much heat energy is required to warm 168 g copper from -12.2 °C to 25.6 °C?
4. If 187 J raises the temperature of 93.45 g of Ag from 18.5 to 27.0°C, what is the specific heat capacity of silver?
5. Find heat energy to warm 168 g copper from -22.2 °C to 25.6 °C?