

# **MME 3514**

# **MATERIALS THERMODYNAMICS**

Fundamentals of Thermodynamics for Systems of Constant Composition

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Thermodynamics addresses two types of problems:

1- Computation of energy difference between two physical conditions

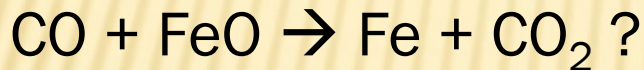
Example- Between coal + oxygen and combustion products

Between gases at different densities

Between pure species and their mixtures

2- Determination of spontaneous direction of a process

Example- Can the top gas from an iron blast furnace containing CO be recycled to reduce more iron oxide?



Will  $\text{H}_2\text{O}$  start to boil at 0.8 atm and 98 °C ?

Will water and ethanol mix completely or separate ?

Problems outside the scope of thermodynamics:

- Determination of the rate of a possible process
- Determination of microscopic mechanisms involved in transformations



# The Concept of State

State – Physical condition of the system as specified by a small set of measurable variables

Microscopic state of the system depends on the masses, velocities, positions, and all modes of motion of all of the constituent particles

In the absence of detailed knowledge, thermodynamics considers the properties of the system which, when determined, define the macroscopic state of the system

Still an enormous amount of information might be required to fix the macroscopic state of the system

Phase Rule introduces a valuable simplification to determine the state of the system such that when a small number of properties are fixed the values of all the rest are fixed

Commonly for a pure substance, only two properties are independent and all other are dependent variables

Intensive variable – microscopic property of matter (temperature, pressure, composition)

Extensive variable – macroscopic property that depends on the quantity of matter (total volume)

Specific property – the ratio of an extensive property to the mass of the system

Various state properties are related to each other with an equation of state

Example – Ideal gas equation of state

$$P = \frac{nRT}{V}$$



Phase: A homogeneous region of matter

Physically separable parts of a mixture containing one or more chemical species

Example – water and ice, oil and water, iron and cementite  
alcohol and water?

An abrupt change in properties occurs at the boundary between phases

The state of a pure homogeneous fluid is fixed when two intensive thermodynamic properties are set at definite values

Presence of more phases decreases the number of independent intensive variables that must be fixed to establish the state of a system

$$F = 2 - \pi + N$$

Gibbs' Phase Rule gives the degrees of freedom of the system

The number of phase rule variables which must be arbitrarily specified in order to fix the intensive state of a system at equilibrium is the difference between the total number of phase rule variables and the number of independent equations that can be written connecting these variables

Phase rule variables for a system containing  $N$  chemical species and  $\pi$  phases in equilibrium:

Temperature  $T$

Pressure  $P$

$N-1$  mole fractions  $X$  for each phase (only  $N-1$  because  $\sum X_i = 1$  )

Total number =  $2 + (N - 1)(\pi)$

Phase equilibrium equations that may be written connecting the phase rule variables:

$$\mu^\alpha_i = \mu^\beta_i = \cdots = \mu^\pi_i \quad (i = 1, 2, \dots, N)$$

Total number =  $(\pi - 1)(N)$

Thus

$$F = 2 + (N - 1)(\pi) - (\pi - 1)(N) = 2 - \pi + N$$



The minimum degrees of freedom for any system is zero  
 $F=0$  means the system is invariant and eqn. becomes

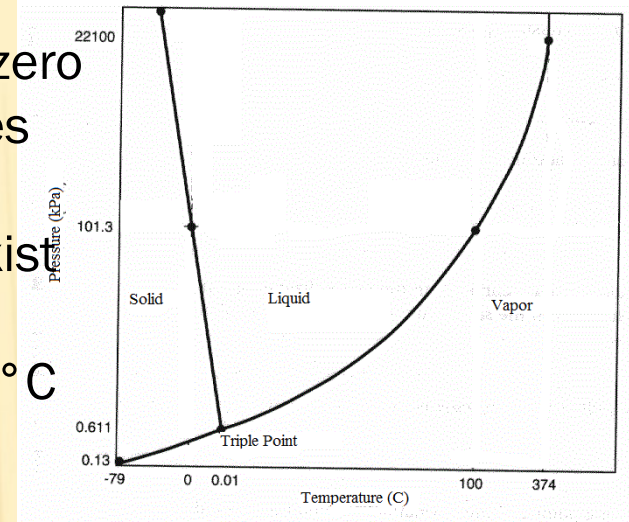
$$F = 2 - \pi + N$$



$$\pi = 2 + N$$

$\pi$  is the maximum number of phases which can coexist at equilibrium for a system containing  $N$  species

Example –  $\pi = 3$  for water at the triple point at  $0.01^\circ\text{C}$  and  $0.00611\text{ bar}$



Independent control on two variables is not possible for a pure substance with two phases in equilibrium

Example

Steam and liquid water can coexist in equilibrium at  $100^\circ\text{C}$  only at  $101.33\text{ kPa}$

Examples – Liquid water in equilibrium with its vapor

$T$  or  $P$  may be specified for a system consisting of water in equilibrium with its vapor

$$F = 2 - 2 + 1 = 1$$

Liquid water in equilibrium with a mixture of water vapor and nitrogen

$$F = 2 - 2 + 2 = 2$$

$T$  and  $P$  may be independently varied for a pure system with the addition of an inert gas, but once they are fixed the system described can exist in equilibrium only at a particular composition  $X$

The first law of thermodynamics states that:

*Although energy has many forms, the total quantity of energy is constant. When energy disappears in one form, it appears simultaneously in other forms*

Hence

$$\Delta U + \Delta E_K + \Delta E_P = Q - W$$

Heat and work are forms of energy that are transformed into other forms of energy. If friction is eliminated, work is efficiently transformed to potential, kinetic, electrical and heat energy by a conversion ratio of upto 100%.

Heat on the other hand is readily lost to the surroundings and its conversion into work, mechanical or electrical energy does not exceed 40% efficiency because the flow of heat always takes place from the hotter to the cooler body and never in the reverse direction

The second law describes the direction of energy transfer in actual processes



Zeroth law of thermodynamics states that

If two bodies are in thermal equilibrium with a third body, they are in thermal equilibrium with each other and hence their temperatures are equal

Specific Heat:

It is the amount of heat required to raise the temperature of a 1 kg mass  $1^{\circ}\text{C}$  or  $1^{\circ}\text{K}$

$$C = \frac{dQ}{dt}$$

$$dQ = CdT$$

by integration

$$Q = C (T_2 - T_1) \frac{\text{KJ}}{\text{kg}}$$

Considering the mass  $m$ ,

$$Q = mC (T_2 - T_1) \text{ KJ}$$

Sensible Heat - The amount of heat that must be added or removed when a substance undergoes a change in temperature without a change in phase

$$Q = mC(T_2 - T_1)$$

Heat of Transformation - The amount of heat that must be transferred when a substance completely undergoes a phase change without a change in temperature.

- Heat of Vaporization: The amount of heat added to vaporize a liquid or amount of heat removed to condense a vapor or gas

$$Q = mL_v$$

where: L – latent heat of vaporization, KJ/kg

m – mass, kg, kg/sec

- Heat of Fusion: It is the amount of heat added to melt a solid or the amount of heat removed to freeze a liquid

$$Q = mL_F$$

where: L – latent heat of fusion, KJ/kg

m – mass, kg, kg/sec



# Thermodynamic Equilibrium

A system is said to be in equilibrium when its observable properties do not change with time as long as the external conditions are unaltered

Thermal equilibrium –  $T$  constant

Mechanical equilibrium –  $P$  constant

Chemical equilibrium – Forward and reverse reaction rates constant

Process – Transformation of a system from one state to another by a change in anyone of the thermodynamic properties of the system

Isothermal process – constant temperature

Isobaric process – constant pressure

Isochovic process – constant volume

Path – Locus of all the states that the system passes through during a reversible process

The points in P-V-T space which represents the equilibrium states of existence of the system lie on a surface

Fixing the values of any two of the three variables fixes the value of the third variable

$$F = 2 - \pi + N$$

$$V = V(P, T)$$

Consider a process which moves the gas from state 1 to state 2

$$\Delta V = V_2 - V_1$$

Process could proceed along an infinite number of paths

1-a, b-2 constant P paths

1-b, a-2 constant T paths

$$dV = \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT$$

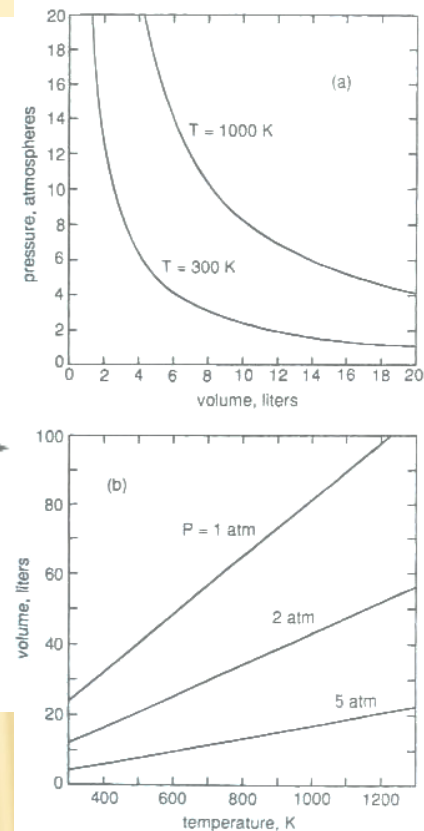
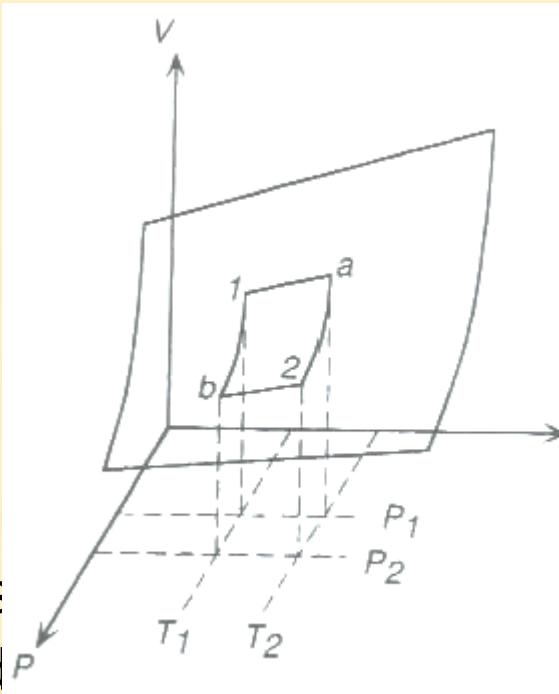


Figure 1.3 (a) The variations, with pressure, of the volume of 1 mole of ideal gas at 300 and 1000 K. (b) The variations, with temperature, of the volume of 1 mole of ideal gas at 1, 2, and 5 atm.



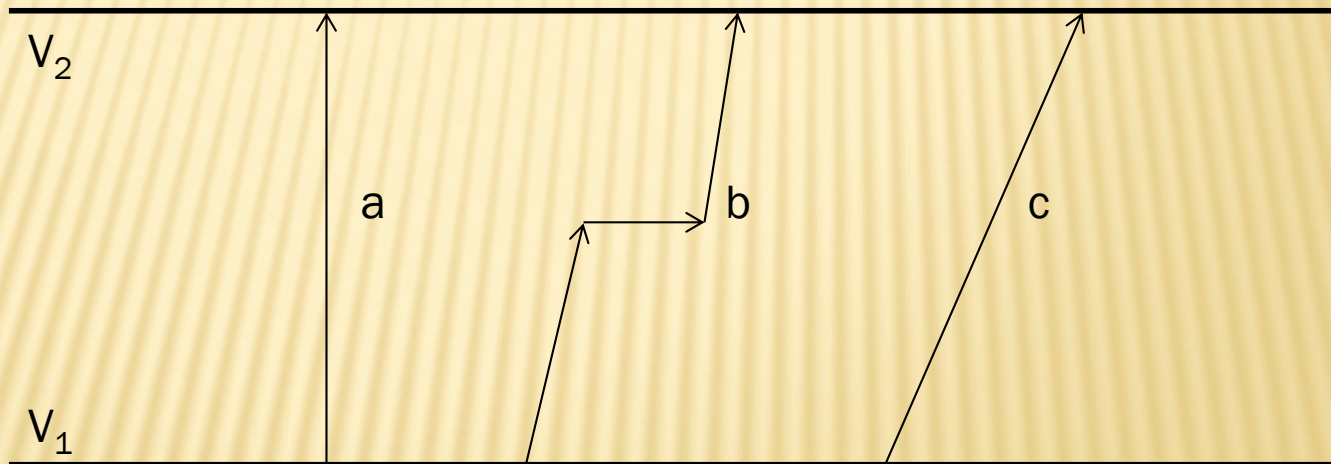
$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

Integrating the complete differential between the limits  $P_2T_2$  and  $P_1T_1$ :

$$\Delta V = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$$

The change in volume depends only on volume at state 1 and volume at state 2 and is independent of the path taken by the gas between states 1 and 2 since  $V$  is a *state function*

State functions have exact differentials



$$\Delta V_a = \Delta V_b = \Delta V_c$$

$$T_a \neq T_b \neq T_c$$

$$P_a \neq P_b \neq P_c$$

Similarly, the first law of thermodynamics introduces another state property, internal energy:

$$\Delta U = Q - W$$

$$dU = \delta Q - \delta W$$

The heat and work effects which involve energy in transit, depend on the path taken between the two states

So their integrals cannot be evaluated without a knowledge of the path

$$dU = \delta Q - \delta W = C_p dT - P dV \quad \text{for constant pressure path}$$

$$dU = \delta Q = C_v dT \quad \text{for constant volume path}$$

$$dU = 0 \quad \text{for isothermal path}$$

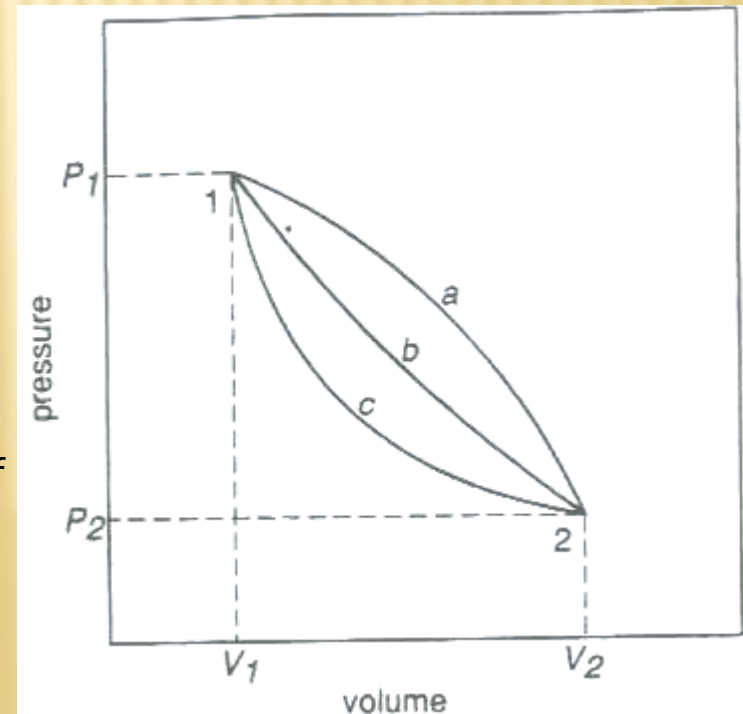
$$\Delta U = \int_{V_1}^{V_2} \left( \frac{\partial U}{\partial V} \right)_P dV + \int_{P_1}^{P_2} \left( \frac{\partial U}{\partial P} \right)_V dP$$

$$\Delta U = \int_{V_1}^{V_2} P_2 dV + \int_{T_1}^{T_2} C_v dT \quad T_1 = \frac{PV_1}{R}$$

Path a+c completes a cycle which changes the state of system back to the original state

So cyclic integral of a state function is zero

$$\oint dU = 0$$





The first law of thermodynamics simplifies accordingly for the special case of constant P:

$$\Delta U = Q - W$$

$$\Delta U = Q - P\Delta V$$

$$Q = \Delta U + P\Delta V \text{ state function}$$

Enthalpy change  $\Delta H = Q$  for a constant P process

$$C = \frac{\delta Q}{dT}$$

$$dH = \delta Q = C_p dT \text{ for constant pressure path}$$

$$dU = \delta Q = C_v dT \text{ for constant volume path}$$

Since  $dH = dU + PdV$ ,  $C_p$  is expected to be greater than  $C_v$

If the temperature of an ideal gas is raised by  $dT$  at constant volume, all of the internal energy change equals the heat gained during the process

However, if the temperature change happens at constant pressure, some energy will be needed to expand the system:

$\frac{PdV}{dT}$  or  $P \left( \frac{\delta V}{\delta T} \right)_P$  more detailed derivation is given in text books

Hence  $C_p - C_v = P \frac{R}{P} = R$  for ideal gases

Ideal gas is defined to behave as a gas with infinite intermolecular distance, negligible intermolecular attraction and zero pressure. Hence, internal energy of an ideal gas is a function of temperature and independent of volume and pressure

For real gases,  $C_p - C_v = \left( \frac{\delta V}{\delta T} \right)_P \left[ P + \left( \frac{\delta U}{\delta V} \right)_T \right]$   
 $\left( \frac{\delta V}{\delta T} \right)_P \left( \frac{\delta U}{\delta V} \right)_T$  represents the work done per degree rise in temperature in expanding against the internal cohesive forces acting between the particles of the gas  
The term is small for gases and large for liquids and solids



Ideal gas is a good approximation to understand and control the work output of steam engines

Consider the reversible adiabatic expansion of an ideal gas

As heat transfer in or out the system is zero, the work done by the system decreases the internal energy

$$dU = -\delta W$$

$$dU = C_v dT$$

$$dW = PdV$$

So

$$C_v dT = -PdV = -\frac{RT}{V}dV$$

integrating yields

$$C_v \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{V_1}{V_2}\right)$$

and

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}}$$

$$\frac{R}{C_v} = \frac{C_p}{C_v} - 1 \quad \text{since} \quad C_p - C_v = R \quad \text{for ideal gases}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2 V_2}{P_1 V_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_p}{C_v} - 1}$$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_p}{C_v}}$$

$$P_1 V_1^{\frac{C_p}{C_v}} = P_2 V_2^{\frac{C_p}{C_v}} = \text{constant}$$

Now consider the reversible isothermal expansion of an ideal gas

Internal energy change of any system is zero when the temperature is constant

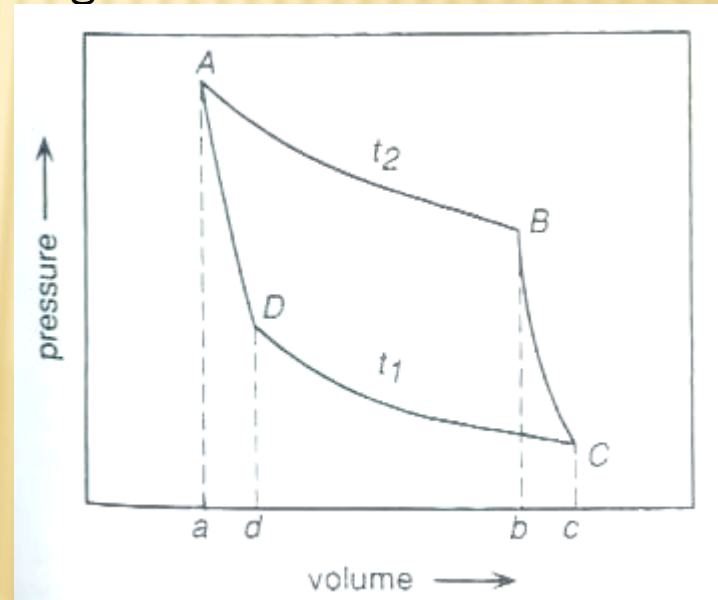
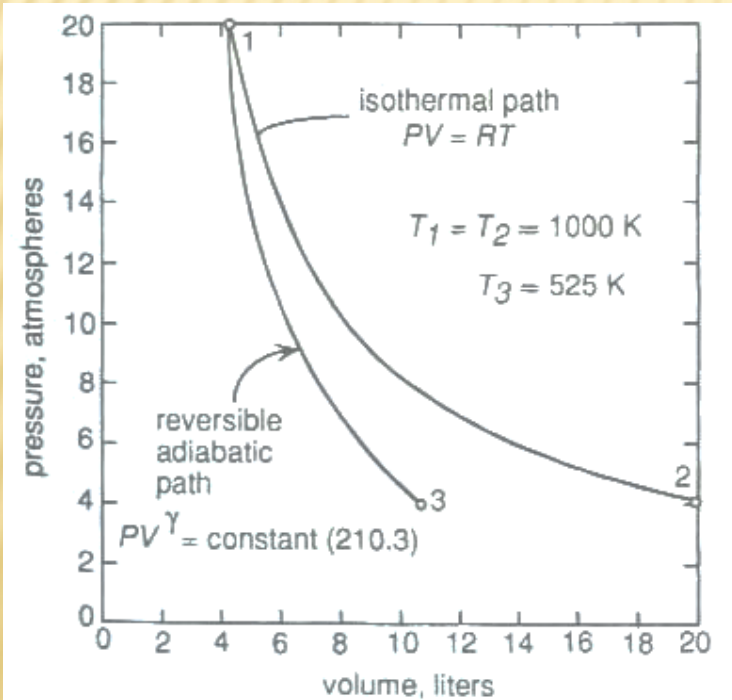
$$\Delta U = 0, \quad \delta Q = \delta W = PdV = \frac{RT}{V} dV$$

$$Q = W = PdV = RT \ln \left( \frac{V_2}{V_1} \right) = RT \ln \left( \frac{P_1}{P_2} \right)$$

since  $P_1V_1 = P_2V_2 = \text{constant}$

The work done by an reversible isothermal process exceeds that of the reversible adiabatic because the internal energy of the adiabatically contained system decreases with work

Isothermal paths are utilized in heat engines to perform higher work





Carnot cycle invented by Sadi Carnot in 1824, led to efficient power generation by the use of thermodynamic principles deduced from the first and second law

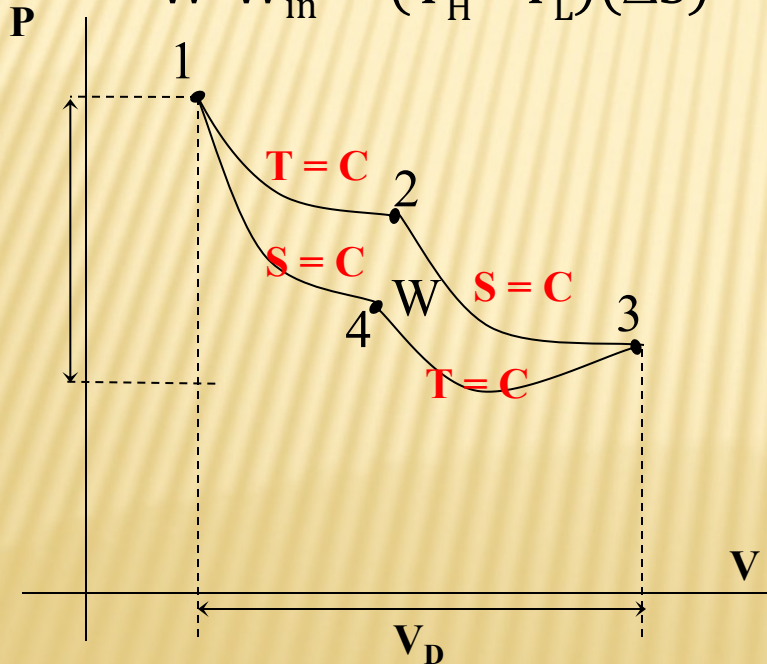
$$\oint dQ = \oint dW$$

$$W = \Sigma Q$$

Net Work Output

$$W - W_{\text{in}} = \Sigma Q = Q_A - Q_R$$

$$W - W_{\text{in}} = (T_H - T_L)(\Delta S)$$



Carnot Cycle Processes:

1 to 2 - Heat Addition ( $T = C$ )  $Q_A = T_H(\Delta S)$

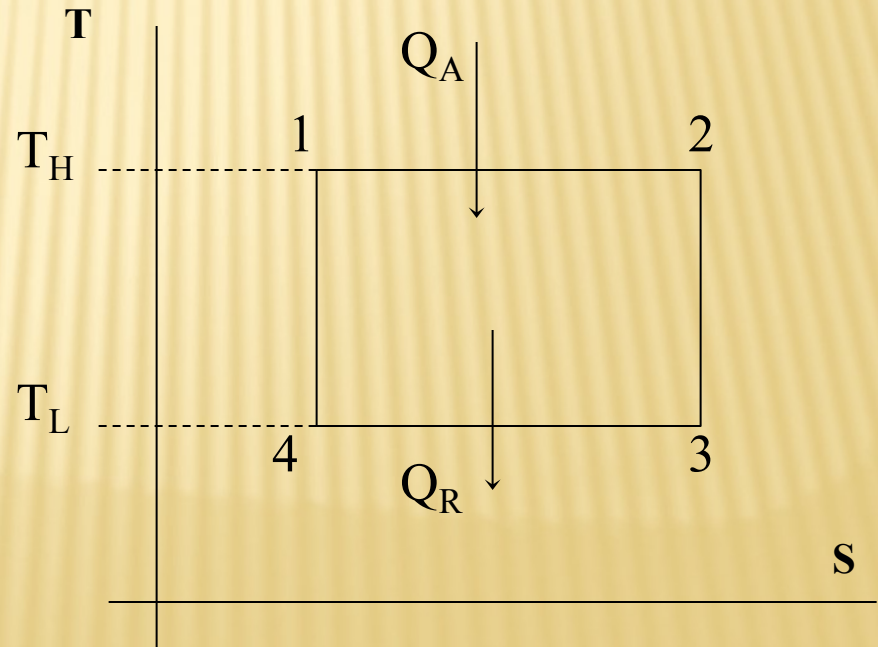
2 to 3 - Expansion ( $S = C$ )

3 to 4 - Heat Rejection ( $T = C$ )

$$Q_R = T_L(\Delta S)$$

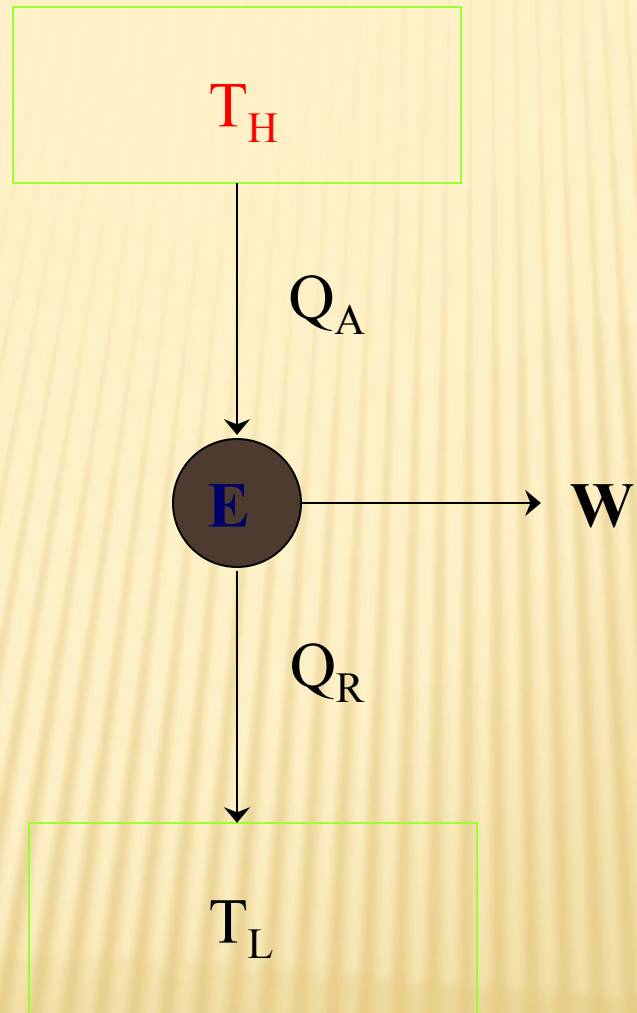
$$\Delta S = S_2 - S_1 = S_4 - S_3$$

4 to 1 - Compression ( $S = C$ )



# Carnot Engine

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The state of a system can also change if chemical identity of constituents are altered by chemical reaction

Thermal effects associated with chemical reactions are estimated to an accurate degree by enthalpy calculations

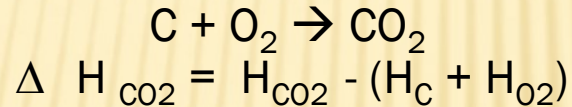
An exothermic reaction supplies heat to the surroundings and has negative enthalpy change

Reactions that require heat input from surroundings are endothermic

Enthalpy change of any reaction can be calculated using Hess' law

$$\Delta H_{\text{RXN}} = \sum \Delta H_{\text{PRODUCTS}} - \sum \Delta H_{\text{REACTANTS}}$$

Example – Compound formation from elements



Since  $\Delta H_{\text{CO}_2} = f(P,T)$ , standard enthalpy of formations are usually tabulated at 298 K under standard atmospheric pressure of 101.33 kPa

$$\Delta H_{298}^{\circ}(\text{CO}_2) = -393690 \text{ J/mole at } 298 \text{ K}$$

Standard enthalpy of formation of pure elements are assigned the value of zero

Hess' law states that enthalpy change accompanying a chemical reaction is the same whether it takes place in one or several stages since enthalpy is a state function

It is useful in calculating the unknown enthalpy change of a reaction using known enthalpy change

## Entropy and the Second law of Thermodynamics

Entropy is that property of a substance that determines the amount of randomness and disorder of a substance. If during a process, an amount of heat is taken and is by divided by the absolute temperature at which it is taken, entropy change is obtained:

$$dS = \frac{dQ}{T}$$

$$dQ = TdS$$

The second law of thermodynamics states that the entropy of the universe increases for spontaneous processes, and the entropy of the universe does not change for reversible processes

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0 \quad \text{reversible processes}$$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0 \quad \text{irreversible processes}$$

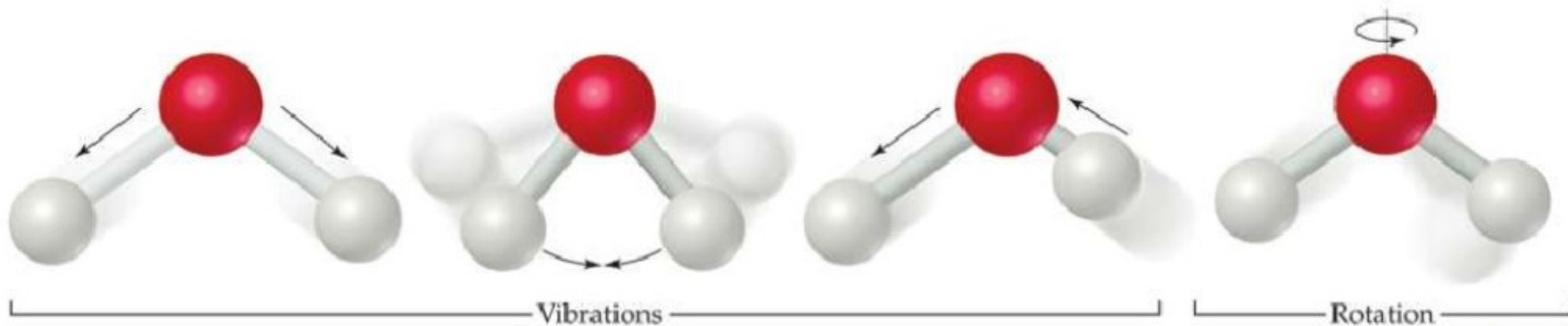
As a result of all spontaneous processes, the entropy of the universe increases



The state of matter with the greatest entropy is gas

Liquids have intermediate entropy and the least disordered state is solid

Entropy in general increases with the freedom of motion of the molecules, so is proportional to temperature, volume and number of independently moving molecules



Ludwig Boltzmann described the concept of entropy on the molecular level

Microstates of matter  $W$ , are referred to as the motions of a sample of molecules at a particular instant of time

$$S = k \log W$$

Translational, vibrational and rotational motions of molecules increase with temperature which is a measure of the average kinetic energy of the molecules in a sample

Thus

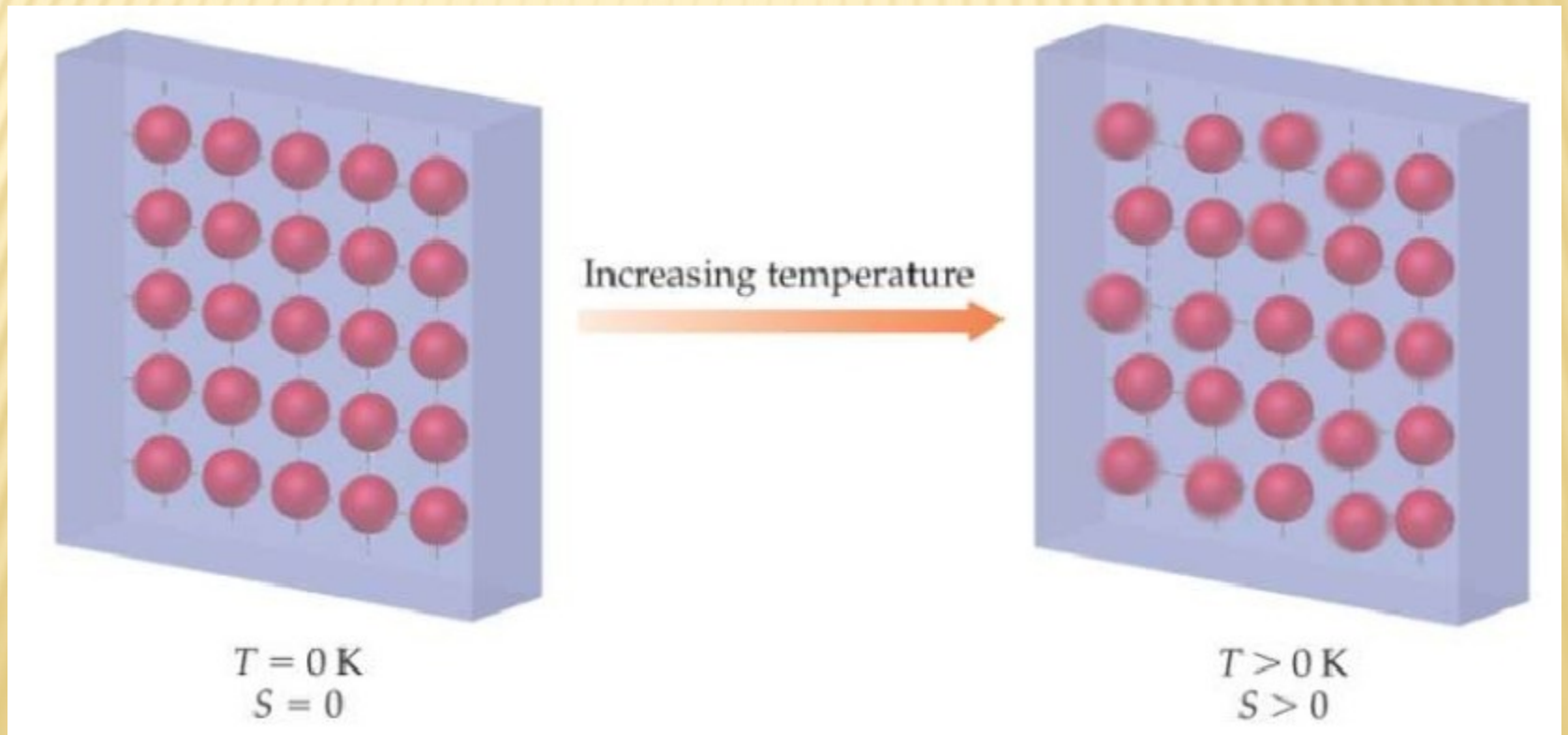
$$\Delta S = k \ln \frac{W_{final}}{W_{initial}}$$

where  $k$  is the Boltzmann constant,  $1.38 \times 10^{-23}$  J/K

Third law of thermodynamics states that the only substance having a perfectly ordered state with zero entropy is a perfect crystal at absolute zero

These extreme conditions can never be met, therefore all substances have some entropy or randomness

from an entropy standpoint, reactions tend to progress towards the formation of gases from liquids and solids and also tend towards forming more molecules from fewer by decomposition, thereby being capable of an even greater disordered condition





## Spontaneity

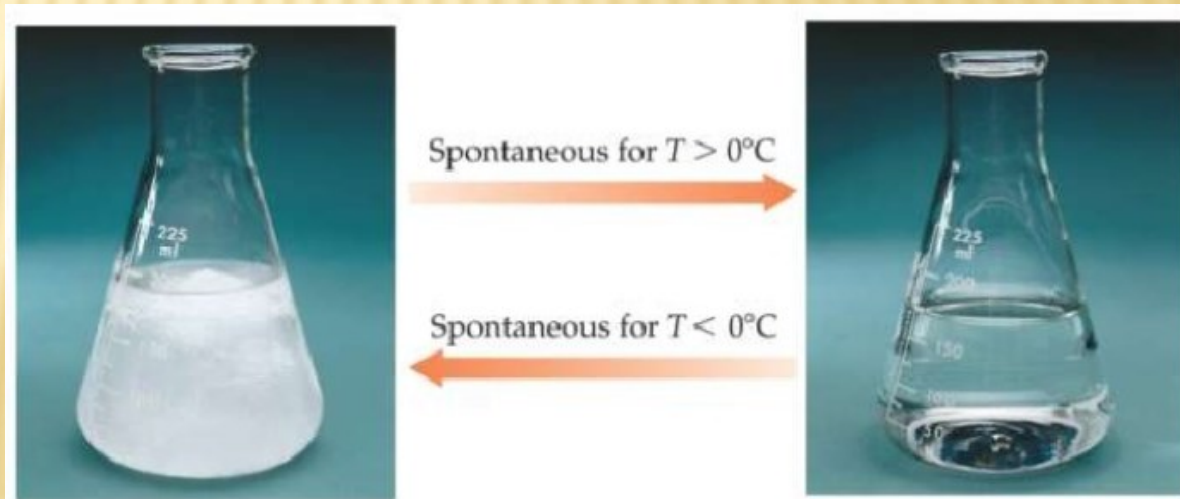
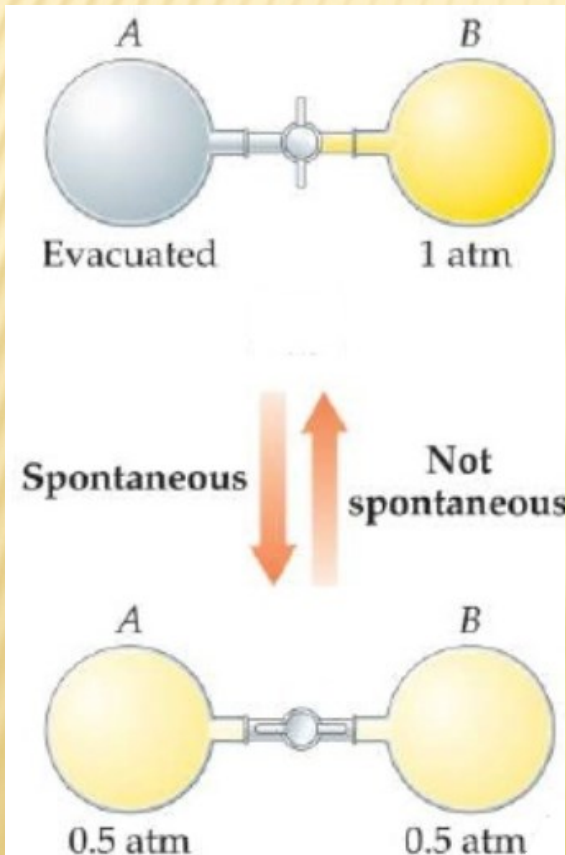
From an energy standpoint, reactions always tend to move in the direction of lowest energy so that exothermic reactions are favored

However, there are numerous instances of spontaneous endothermic reactions

The explanation of this contradiction is provided by the concept known as entropy

All processes have a natural tendency to progress to states of increased entropy or disorder

$$\Delta G = \Delta H - T\Delta S$$



## Gibbs free energy and reaction spontaneity

$$\Delta G = \Delta H - T \Delta S$$

Gibbs – Helmholtz equation

$\Delta G$  = Gibbs free energy (kJ/mole)

$\Delta H$  = Enthalpy change (kJ/mole)

$\Delta S$  = Entropy change (joules/mole)

T = Kelvin temperature (always +)

if  $\Delta S$  for a reaction is (+) the reaction is favored by entropy increasing

if  $\Delta H$  is (-) the reaction is favored by enthalpy decreasing

so  $\Delta G = (-) - (+)(+) = (-)$ , since both entropy and enthalpy drive the reaction toward spontaneity the reaction must be spontaneous forward

Thus a negative  $\Delta G$  indicates a spontaneous forward reaction

$\Delta G = -$  (forward reaction is spontaneous)

$\Delta G = +$  (forward reaction is nonspontaneous)

$\Delta G = 0$  (reaction is at equilibrium)

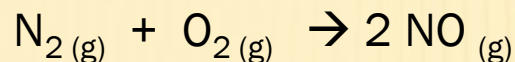
$\Delta G^0$  may be calculated in two ways.

(1)  $\Delta G = \Delta H - T \Delta S$

(2)  $\Delta G^0 = \sum \Delta G^0_{\text{products}} - \sum \Delta G^0_{\text{reactants}}$



Example - Is the reaction spontaneous at 25 °C with 1 atm pressures?



Given data:  $\Delta H^0$  for  $\text{NO}_{(g)} = 21.57 \text{ Kcal/mole}$

$S^0$  for  $\text{NO}_{(g)} = 50.347 \text{ cal/K}$ ,  $S^0$  for  $\text{N}_{2(g)} = 45.77 \text{ cal/K}$

$S^0$  for  $\text{O}_{2(g)} = 49.003 \text{ cal/K}$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta S^0 = \sum S_{\text{PRODUCTS}} - \sum S_{\text{REACTANTS}}$$

$$\Delta S^0 = (2 \times 50.347) - (45.77 + 49.003) = 5.92 \text{ cal/K}$$

$$\Delta H^0 = \sum \Delta H_{\text{PRODUCTS}} - \sum \Delta H_{\text{REACTANTS}}$$

$$\Delta H^0 = (2 \times 21.57) - (0 + 0) = 43.14 \text{ Kcal/mole}$$

$$\Delta G^0 = 43.14 - (298)(0.00592) = + 41.38 \text{ Kcal/mole}$$

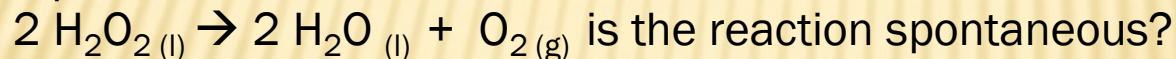
$\Delta G^0$  is + and the reaction is not spontaneous at standard conditions

## Deciding on reaction spontaneity without calculation

The signs of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  can be used to decide on the spontaneity of reactions as well as the temperature dependence of a reaction

| $\Delta H$ | $T_K$ | $\Delta S$ | $\Delta G$ | Reaction Direction        |
|------------|-------|------------|------------|---------------------------|
| -          | +     | +          | -          | SPONT AT ALL TEMPS        |
| +          | +     | -          | +          | NON SPONT AT ALL TEMPS    |
| -          | +     | -          | + / -      | SPONTANEOUS AT LOW TEMPS  |
| +          | +     | +          | + / -      | SPONTANEOUS AT HIGH TEMPS |

Example: If  $\Delta H = -46.9 \text{ Kcal}$  for the reaction:



Since  $\Delta H$  is temperature independent the reaction is exothermic at all temperatures and is favored by lower energy

Two liquid molecules convert to two liquid and a gas molecule and is therefore favored by increasing entropy

Both lower enthalpy ( $\Delta H$  is negative) and increasing entropy ( $\Delta S$  is positive) favor the forward reaction and the reaction is sure to be spontaneous at all temperatures



## General criteria for spontaneity and equilibrium

For all naturally occurring processes  $\Delta S_{\text{Total}}$  is positive

More appropriate criteria for engineering purposes have been introduced:

Constant S and V processes

$$dU = TdS - PdV$$

$\Delta S_{\text{sys}}=0$ ,  $\Delta S_{\text{sur}} = -\Delta U_{\text{sys}}/T$ , hence  $\Delta U_{\text{sys}} < 0$  for spontaneity  
 $\Delta U < 0$  for spontaneity,  $\Delta U = 0$  for equilibrium

Constant T and P processes

$$dG = VdP - SdT$$

$\Delta G < 0$  for spontaneity,  $\Delta G = 0$  for equilibrium

Constant S and P processes

$$dH = TdS + VdP$$

$\Delta H < 0$  for spontaneity,  $\Delta H = 0$  for equilibrium

Constant T and V processes

$$dA = -PdV - SdT$$

$\Delta A < 0$  for spontaneity,  $\Delta A = 0$  for equilibrium