

## Chemical Thermodynamics

*Thermodynamics studies the interrelationships of the various equilibrium properties of a system and the changes in equilibrium properties in processes*

*It studies energy and its transformation into heat and work.*

*In thermodynamics, the universe is comprised of 2 components:*

*system & its surroundings.*

**Main objective** of thermodynamics is to be able to determine if a reaction will occur when reactants are brought together under certain conditions.

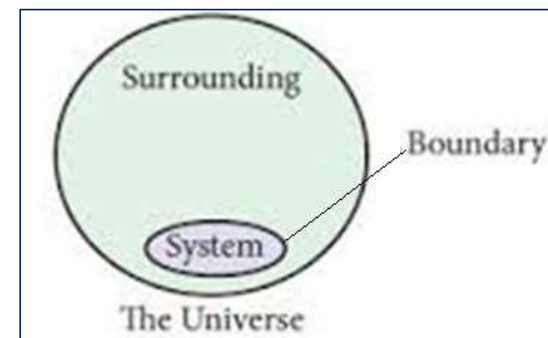
*The **system** may be a reaction vessel, an engine, a biological cell or an electrochemical cell.*

*The **surroundings** refer to the region outside the system and are used for analyses.* Everything that interacts with the system

*A **diathermic** boundary is a boundary that permits the passage of energy as heat, whereas an **adiabatic** boundary is a boundary that prevents the passage of energy as heat.*

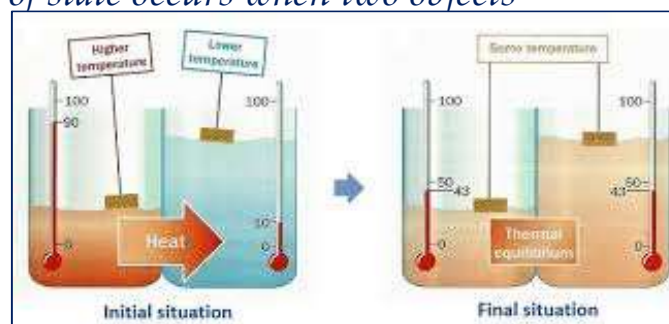
***Thermal equilibrium** is a condition in which no change of state occurs when two objects*

*A and B are in contact through a diathermic boundary.*



A system is a region containing energy and/or matter that is separated from its surroundings by arbitrarily imposed walls or boundaries

A boundary is a closed surface surrounding a system through which energy and mass may enter or leave the system.



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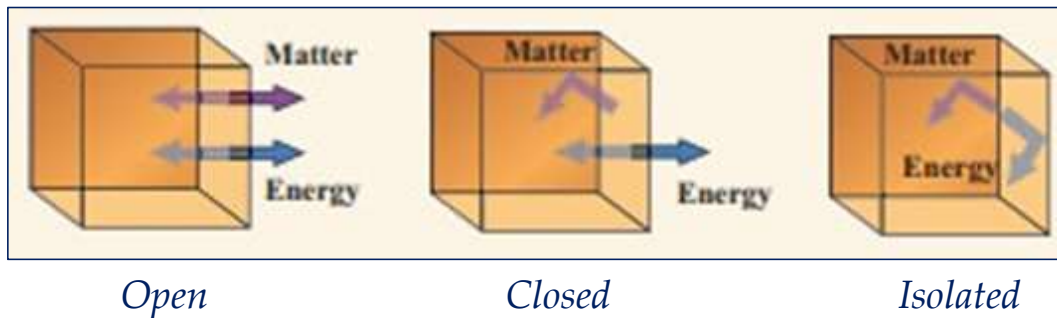
## Types of Systems

The type of system is said to be

- **open** depending upon the possibility of mass transfer between the system and its surroundings through the boundary
- **closed** depending upon the lack of mass transfer between the system and its surroundings through the boundary.

Exchange of energy with the surroundings is possible in both open and closed systems.

- An isolated system (total universe) does not permit exchange of energy.



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## Thermodynamic Processes

When a thermodynamic system undergoes a change of state, we say it has undergone a process.

In a **cyclic process**, the system's final state is the same as the initial state. In a cyclic process, the change in each state function is zero:  $0 = \Delta T = \Delta P = \Delta V = \Delta U = \Delta H$ , etc. However,  $q$  and  $w$  need not be zero for a cyclic process.

In a **reversible process**, the system is always infinitesimally close to equilibrium, and an infinitesimal change in conditions can restore both system and surroundings to their initial states. To perform a process reversibly, one must have only infinitesimal differences in pressures and temperatures, so that work and heat will flow slowly. Any changes in chemical composition must occur slowly & reversibly; moreover, there must be no friction. Work in a mechanically reversible process is given by  $dw_{rev} = -P dV$ .

**Melting and freezing of a substance at its melting point are reversible.**

**Boiling and condensation of a substance at its boiling point are also reversible.**

**Reversible processes are not spontaneous.**

Heat energy is lost to dissipation and that energy will not be recoverable if the process is reversed.

- Irreversible processes cannot be undone by exactly reversing the change to the system.
- The system can go back but the surroundings are changed.
- Spontaneous processes are irreversible.

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- In an **isothermal process**,  $T$  is constant throughout the process. To achieve this, one encloses the system in thermally conducting walls and places it in a large constant temperature bath. For a perfect gas,  $U$  is a function of  $T$  only, so  $U$  is constant in an isothermal process; this is not necessarily true for systems other than perfect gases.
  - In an **adiabatic process**,  $dq = 0$  &  $q = 0$ , achieved by surrounding the system with adiabatic walls.
  - In a **constant-pressure (isobaric) process**,  $P$  is held constant throughout the process.
  - In a **constant-volume (isochoric) process**,  $V$  is held constant throughout the process.
- Here, the system is enclosed in rigid walls. Provided the system is capable of only  $P$ - $V$  work, the work  $w$  is zero in an isochoric process.

<b>1) constant temperature</b> $\Delta U = 0$ isothermal
<b>2) no heat transfer</b> $Q = 0$ adiabatic
<b>3) no pressure change</b> no changes to equation isobaric
<b>4) constant volume</b> $W = 0$ isovolumetric

The main processes in chemical thermodynamics are:

- isobaric-isothermal ( $P, T = \text{const}$ )
- isochoric-isothermal ( $V, T = \text{const}$ )

An **exothermic process** is a process that releases energy as heat into its surroundings. e.g. combustion.

An **endothermic process** is a process in which energy is absorbed from its surroundings as heat. E.g. vaporization.

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## Laws of Thermodynamics

*Each of the first three laws of thermodynamics leads to the existence of a state function.*

*The zeroth law leads to temperature (T).*

*The first law leads to internal energy (U).*

*The second law leads to entropy (S).*

*The third law of thermodynamics concerns the entropy of perfectly-ordered crystals at zero degree kelvin.*

*Zeroth law of thermodynamics is so called because only after the first, second, and third laws of thermodynamics had been formulated was it realized that the zeroth law is needed for the development of thermodynamics. The Zeroth Law of Thermodynamics: states that if two systems are each found to be in thermodynamic equilibrium with a third system, the two original systems are in thermal equilibrium with each other.*

*If system A is in thermal equilibrium with system C and system B is also in thermal equilibrium with system C, system A and system B are in thermal equilibrium with each other.*

*Temperature indicates the direction of the flow of energy through a thermally conducting, rigid wall.*

*The Celsius and thermodynamic temperature scales are related by  $T/K = \theta/^{\circ}\text{C} + 273.15$  [ $^{\circ}\text{K}$  is not used now as Kelvin is absolute scale].*

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## First Law of Thermodynamics

It is deduced experimentally that internal energy of a system may be changed either by heating a system or by doing work on it. Therefore, the First Law of Thermodynamics can be defined as:

**Energy can neither be created nor destroyed; it may only be converted from one form to another.**

**OR The total energy of an isolated system remains constant.**

The two forms of the first law of thermodynamics is as follows

In a closed system,  $dU = dq + dw$        $\Delta U = q + w$

where  $U$ /  $E$  is the internal energy of the system, a state function;  
 $q$  is heat; and  $w$  is thermodynamic work.

The equation  $dU = dq + dw$  is the differential form of the 1st law,  
 &  $\Delta U = q + w$  is the integrated form.

Expansion work is work

arising from change in volume.

$$\Delta E = q + w$$

$$w = P\Delta V$$

$$\Delta E = q + P\Delta V$$

$$\Delta E = q + \Delta nRT$$

**(U)** of a thermodynamic system is the total kinetic energy due to the motion of molecules (translational, rotational, vibrational) and the potential energy associated with the vibrational and electric energy of atoms within molecules and crystals.

For $q$	+ means system gains heat	– means system loses heat
For $w$	+ means work done on system	– means work done by system
For $\Delta E$	+ means net gain of energy by system	– means net loss of energy by system

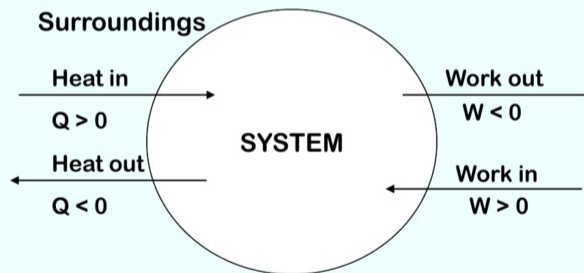
**E = internal energy** = sum of all potential and kinetic energy of the system:

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

### 1. First Law of Thermodynamics (Conservation of energy)

$$\Delta E = q + w$$

where,  $q$  = heat absorbed by system  
 $w$  = work done on system



#### Sign Conventions:

$Q(+)$  --> System absorbs heat

$W(+)$  --> work done on system

$E$  is a "state function" -- independent of pathway, but,  $q$  and  $w$  are not! (they do depend on pathway)

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From the first law of thermodynamics, it is clear that

- 1. Work and heat are mutually interconvertible forms of energy
- 2. Appearance of one form of energy indicates the disappearance of an equivalent form of another form of energy.

**Limitations of the first law of thermodynamics:**

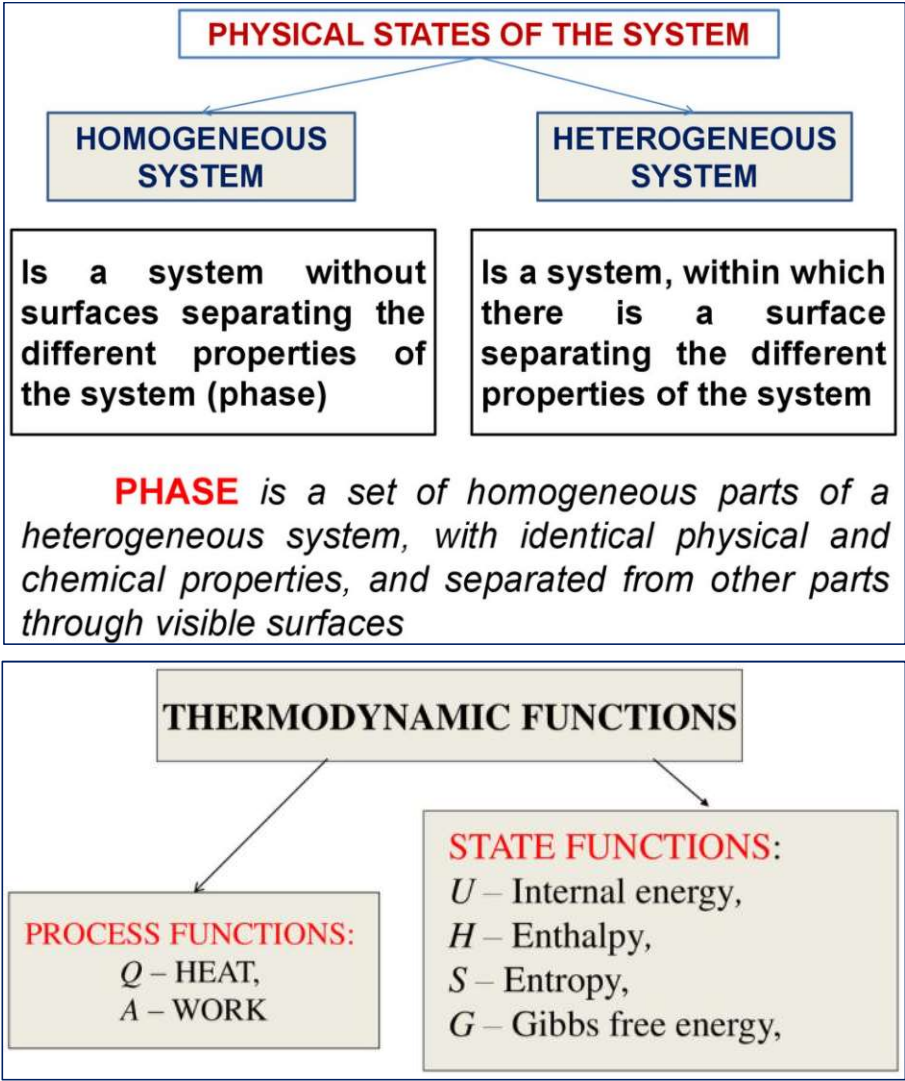
- 1. What would be the direction of energy transformation.
- 2. To what extent transformation would take place.

These insufficiencies are remedied by introducing the 2nd law.

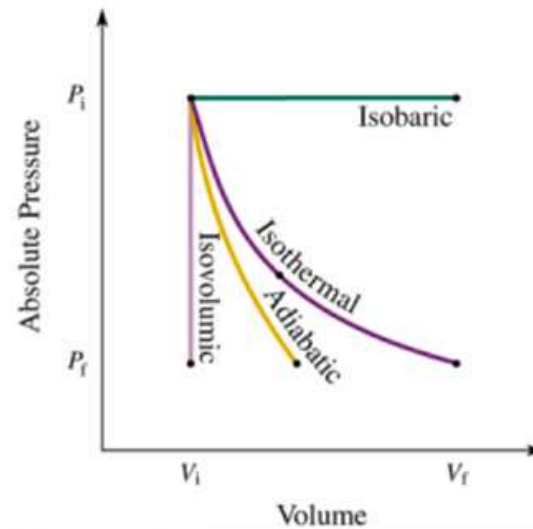
**THERMODYNAMIC FUNCTIONS**

Derivative quantities, dependent on the parameters of the system state and immeasurable by direct methods are called thermodynamic functions:

In thermodynamics, **state function** is a property of a system that depends only on the current state of the system, not on the way in which the system acquired that state. A state function describes the equilibrium state of a system. work and heat are not properties of the system, they characterize the process of energy exchange between the system and the surroundings, therefore they depend on the path (specific transition) of the process.



$$\Delta U = Q - W$$



*The work done on or by a system undergoing a thermodynamic process can be determined by finding the area enclosed by the corresponding pressure–volume curve.*

Variable	Positive Value	Negative Value
Change in Internal Energy ( $\Delta U$ )	Increasing temperature	Decreasing temperature
Heat ( $Q$ )	Heat flows into system	Heat flows out of system
Work ( $W$ )	Work is done by the system (expansion)	Work is done on the system (compression)

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## Heat, Work and Energy

The heat and work appearing in the first law are two different modes of energy transfer. Heat and work are defined only in terms of processes. Before and after energy transfer between system and surroundings, heat and work do not exist.

**Heat:** is an energy transfer between system and surroundings due to a temperature difference.

**Work:** is an energy transfer between system and surroundings due to a macroscopic force acting through a distance.

Work done by a perfect gas for reversible isothermal expansion is equal to area under the isotherm,  $P = nRT/V$ ,  $V = V_f - V_i$

R: Gas constant,  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

**Energy:** of a system is its capacity to do work or to transfer heat.

Heat and work are forms/measures of energy transfer rather than forms of energy, and both have the same units as energy. The unit of heat can therefore be defined in terms of the joule. Thus definition of the calorie is  $1 \text{ cal} = 4.184 \text{ J}$ .

An energy of **1 cal** is defined as the energy required to raise the temperature of 1 g of water by  $1^\circ\text{C}$ . Other units are also used for energy: **1 electronvolt (1 eV)** is defined as the kinetic energy acquired when an electron is accelerated from rest through a potential difference of 1 V; the relation between electronvolts and joules is  $1 \text{ eV} \approx 0.16 \text{ aJ}$  ( $1 \text{ aJ} = 10^{-18} \text{ J}$ ).

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**The enthalpy H:** is the thermodynamic function that accounts for the heat released/absorbed by a process occurring at constant pressure when no additional forms of work are performed. The enthalpy  $H$  of a thermodynamic system whose internal energy, pressure, and volume are  $U$ ,  $P$ , and  $V$  is defined as  $H = U + PV$ . Since  $U$ ,  $P$ , and  $V$  are state functions,  $H$  is a state function (whose value depends only on the current state of the system and is independent of path of the process).

In enthalpy,  $\Delta H$  between initial and final states is independent of the path between them and equal to the energy supplied as heat at constant pressure (provided the system does no additional work). A constant-pressure process is mechanically reversible because if there are unbalanced mechanical forces acting on the system, the system's pressure  $P$  would not remain constant.

An enthalpy change can be measured by monitoring the temperature change that accompanies a physical or chemical change taking place at constant pressure. A calorimeter for studying processes at constant pressure is called an **isobaric calorimeter**. An **adiabatic flame calorimeter** (for a combustion reaction) or **differential scanning calorimeter** (DSC) may also be used.

$dH = dq$  (at constant  $P$ , no additional work)  $q_p$ : the heat absorbed in a constant-pressure process in a closed system. For measurable change,  $\Delta H = q_p$  Most chemical reactions occur at constant pressure, thus

Heat transferred at constant $P = q_p$	
$q_p = \Delta H$	where $H = \text{enthalpy}$

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### Justification:

For a general infinitesimal change in the state of the system,  $U$  changes to  $U + dU$ ,  $p$  changes to  $p + dp$ , and  $V$  changes to  $V + dV$ , so from the definition of enthalpy,  $H$  changes from  $U + pV$  to

$$\begin{aligned} H + dH &= (U + dU) + (p + dp)(V + dV) \\ &= U + dU + pV + pdV + Vdp + dpdV \end{aligned}$$

The last term is the product of two infinitesimally small quantities and can therefore be neglected. As a result, after recognizing  $U + pV = H$  on the right, we find that  $H$  changes to

$$H + dH = H + dU + pdV + Vdp \text{ and hence } dH = dU + pdV + Vdp$$

Substituting the first law  $dU = dq + dw$  into this expression, we get

$$dH = dq + dw + pdV + Vdp$$

If the system is in equilibrium with its surroundings at a pressure  $p$  and does only expansion work, we can write  $dw = -pdV$  and obtain

$$dH = dq + Vdp$$

Now we impose the condition that the heating occurs at constant pressure by writing  $dp = 0$ . Then  $dH = dq$  (at constant pressure, no additional work)

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Heat capacity  $C_{pr}$  of a closed system for an infinitesimal process  $pr$  is defined as  $C_{pr} = dq_{pr}/dT$ , where  $dq_{pr}$  and  $dT$  are heat flowing into the system and temperature change of the system in the process. For a constant-pressure process we get  $C_p$ , the heat capacity at constant pressure (or isobaric heat capacity):

$$C_p = dq_p/dT \quad \text{or} \quad c_p \equiv \left( \frac{\partial h}{\partial T} \right)_p$$

Heat capacity at constant pressure  $C_p$  and at constant volume  $C_v$  are extensive properties.

An **extensive property** is one that depends on amount of substance in the sample (mass, V).

An **intensive property** is a property that is independent of the amount of substance in the sample. E.g. temperature, pressure, mass density (ratio of mass by volume).

The **molar heat capacity at constant pressure**,  $C_{p,m}$  is the heat capacity **per mole of material**; an intensive property. For a real gas an approximation to the empirical expression is  **$C_{p,m} = a + bT + c/T^2$** , (empirical parameters  $a$ ,  $b$ , and  $c$  are independent of temp & experimentally validated).

For infinitesimal changes of temperature,  $dH = C_p dT$  (at constant pressure).

For a measurable increase in temperature  $\Delta H = C_p \Delta T$  (at constant pressure)

Increase in enthalpy can be equated with energy supplied as heat at constant pressure  $q_p C_p \Delta T$

Similarly, the heat capacity at constant volume (or isochoric heat capacity)  $C_v$  of a closed system is

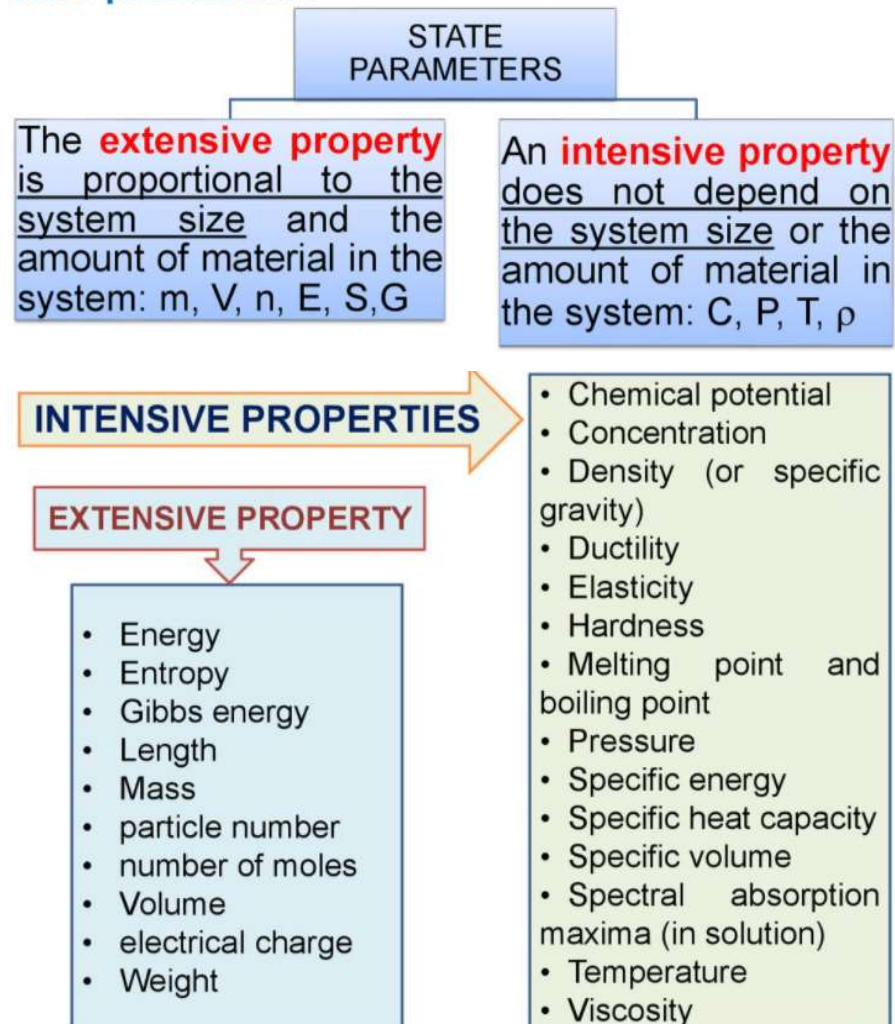
$$C_v = dq_v/dT \quad \text{or} \quad c_v \equiv \left( \frac{\partial u}{\partial T} \right)_v$$

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All quantities characterizing any macroscopic property of the system is called state parameters.



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Heat capacity is more if the substance has more number of atoms, and it has more extent of intermolecular forces.

- $C_p - C_v = R$

- The ratio,  $C_p / C_v$  is known as **Poisson's ratio** and is represented by  $\gamma$ .

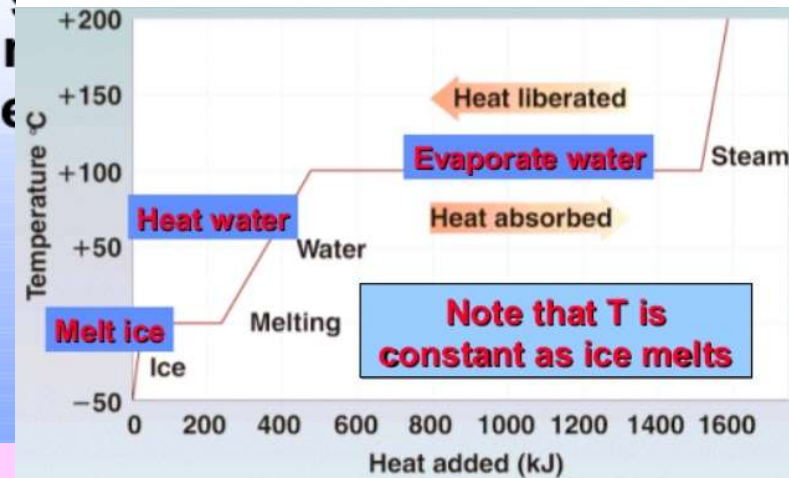
- $\gamma = 5/3 = 1.66$  for mono atomic gases,

- $\gamma = 7/5 = 1.4$  for diatomic gases,

- $\gamma = 9/7 = 1.33$  for polyatomic gases.

Specific heat capacity =

$$\frac{\text{heat lost or gained by substance}}{(\text{mass, g})(T \text{ change, K})}$$



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$$C_P - C_V = \left( \frac{\partial H}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial(U + PV)}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V$$

$$C_P - C_V = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V$$

*In  $(\partial U / \partial T)_V$  is a function of T and V. Thus,  $U=U(T,V)$ . Therefore, the total differential of  $U(T,V)$  is*

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

*At constant P, the equation becomes*

$$dU_P = \left( \frac{\partial U}{\partial T} \right)_V dT_P + \left( \frac{\partial U}{\partial V} \right)_T dV_P$$

*Dividing by  $dT_P$  gives*

$$\frac{dU_P}{dT_P} = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \frac{dV_P}{dT_P}$$

*The ratio of infinitesimals  $dU_P/dT_P$  is the partial derivative  $(\partial U / \partial T)_P$ ,*

$$\left( \frac{\partial U}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P$$

*Which finally becomes*

$$C_P - C_V = \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \left( \frac{\partial V}{\partial T} \right)_P$$

*Relationship between  $C_p$  and  $C_V$  for ideal gas:  $C_p - C_V = nR$  [ $PV=nRT$ ]*

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For the reversible adiabatic expansion of a perfect gas, pressure and volume are related by an expression that depends on the ratio of heat capacities. The change in internal energy of a perfect gas when the temperature is changed from  $T_i$  to  $T_f$  is

$$\Delta U = C_V(T_f - T_i) = C_V\Delta T$$

Since expansion here is adiabatic, we know that  $q = 0$ ; from 1<sup>st</sup> law,  $\Delta U = q + w$ , therefore  $\Delta U = w_{ad}$ .

Equating the two,  $w_{ad} = C_V\Delta T$

For a perfect gas undergoing reversible adiabatic expansion,  $T_f = T_i (V_i/V_f)^{1/c}$

where  $c = C_{V,m}/R$ , so  $V_i T_i^c = V_f T_f^c$

This is summarized as  $VT^c = \text{constant}$ .

For the reversible adiabatic expansion of a perfect gas,

$$p_f V_f^\gamma = p_i V_i^\gamma$$

where  $\gamma = C_{p,m}/C_{V,m}$ . This is summarized as  $pV^\gamma = \text{constant}$ .

*Changes in enthalpy under standard conditions:*

The **standard enthalpy change**,  $\Delta H^\ominus$ , the change in enthalpy for a process in which the initial and final substances are in their standard states.

**The standard state of a substance at a specified temperature is its pure form at 1 bar.**

The **standard enthalpy of transition** is the standard enthalpy change that accompanies a change of physical state and is denoted by  $\Delta_{\text{trs}}H^\ominus$ : (as in fusion, vaporization, sublimation, combustion, ionization, atomization, solution, hydration, activation, formation, etc.)

**Enthalpies of physical change:**

The **standard enthalpy of fusion**,  $\Delta_{\text{fus}}H^\ominus$ , the standard enthalpy change is the enthalpy change per mole when a pure solid at 1 bar fuses into a liquid at 1 bar.  $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)} \quad \Delta_{\text{fus}}H^\ominus(273 \text{ K}) = +6.01 \text{ kJ mol}^{-1}$

The **standard enthalpy of vaporization**,  $\Delta_{\text{vap}}H^\ominus$ , is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar.  $\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)} \quad \Delta_{\text{vap}}H^\ominus(373 \text{ K}) = +40.66 \text{ kJ mol}^{-1}$

When the vaporization of an ionic solid involves a large increase in energy to break strong Coulombic

interactions of the ions, **the lattice enthalpy**,  $\Delta H_L$ , is the change in molar enthalpy for this process



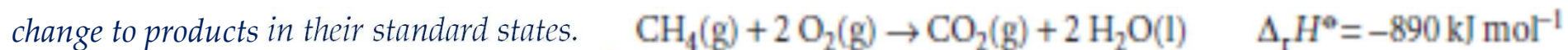
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## Enthalpies of chemical change:

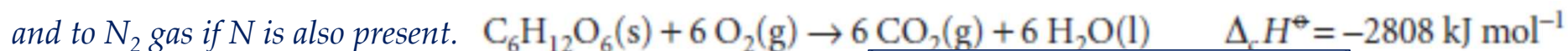
The **standard reaction enthalpy**  $\Delta_r H^\ominus$  is the change in enthalpy when reactants in their standard states change to products in their standard states.



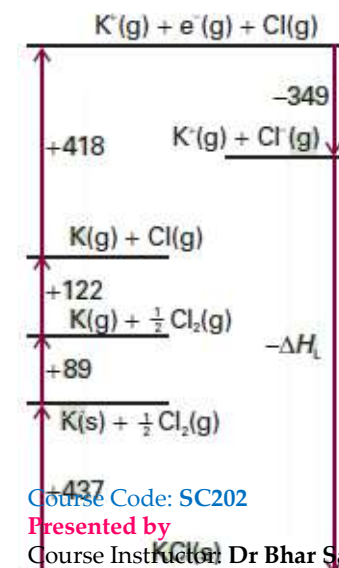
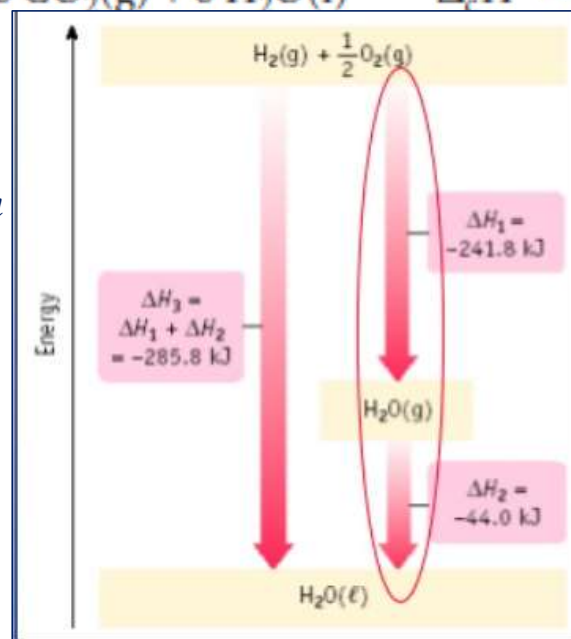
For any reaction,  $\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_m^\ominus - \sum_{\text{Reactants}} \nu H_m^\ominus$

where, the molar enthalpies of the respective species are multiplied by their stoichiometric coefficients,  $\nu$ .

The **standard enthalpy of combustion**,  $\Delta_c H^\ominus$ , is the standard reaction enthalpy for the complete oxidation of an organic compound to  $\text{CO}_2$  gas and liquid  $\text{H}_2\text{O}$  if the compound contains C, H, and O,



Experimental values of lattice enthalpy are obtained from the **Born–Haber cycle**, a closed path of transformations starting and ending at the same point, one step of which is the formation of the solid compound from a gas of widely separated ions.



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Standard enthalpies of individual reactions can be combined to obtain the enthalpy of another reaction.

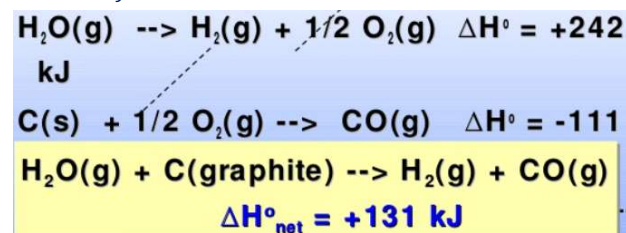
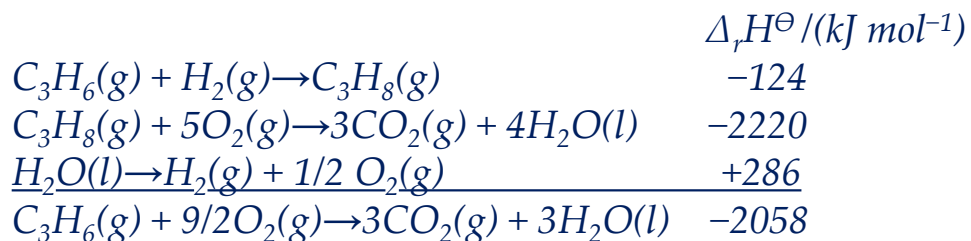
This particular application of the First Law is called **Hess's law**:

**The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.**

The individual steps may not be practically possible i.e. they may be hypothetical reactions, however, their chemical equations should balance.

Importance of Hess's law: For a reaction of interest, which may be difficult to determine directly, enthalpy can be assembled from information on other reactions.

The standard reaction enthalpy for the hydrogenation of propene is  $-124 \text{ kJ mol}^{-1}$ . The standard reaction enthalpy for the combustion of propane, is  $-2220 \text{ kJ mol}^{-1}$ . Thus,



To convert 1 mol of water to 1 mol each of  $\text{H}_2$  and CO **requires** 131 kJ of energy.  
The "water gas" reaction is **ENDO**thermic

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## Second law of thermodynamics

The second law of thermodynamics concerns entropy and the spontaneity of processes.

Entropy is a measure of the energy that becomes dissipated and unavailable (friction, molecular motion = heat)

The law can be stated as follows:

*It is impossible for a heat engine that operates on a cycle to convert the heat absorbed completely into a net amount of work.*

*Heat cannot, of itself, pass from a cold body to a hot body. OR*

*The entropy of any isolated system never decreases. An isolated system evolves towards thermodynamic equilibrium — the state of maximum entropy of the system.*

The mathematical statement of the second law is given below:

$S = \int \delta q / T_b$  for a reversible change of a closed system;

$dS > \delta q / T_b$  for an irreversible change of a closed system;

where  $S$  is an extensive state function, the entropy, and

$\delta q$  is an infinitesimal quantity of energy transferred by heat at a portion of the boundary where the thermodynamic temperature is  $T_b$ ,  $1/T_b$  is called integrating factor for  $\delta q$ .

$$\Delta S_{(\text{surroundings})} = -q_{\text{sys}} / T = -(\Delta H / T)$$

Entropy is associated with randomness. The entropy,  $S$ , of a system is a state function just like the internal energy. The change in entropy is given by

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Entropy ( $S$ ) increases with the number of energetically equivalent ways to arrange the components of a system to achieve a particular state.

*Trends:*

- In general:  $S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$
- larger mass  $\Rightarrow$  more entropy
- more complex structure  $\Rightarrow$  more entropy
- more atoms in molecule  $\Rightarrow$  more entropy

### Second Law of Thermodynamics

“...for any spontaneous process, the overall entropy of the universe increases...”

A spontaneous process can have a negative  $\Delta S$  for the system only if the surroundings have a larger positive  $\Delta S$ .

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\text{where } \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

At constant pressure,  $q_{\text{sys}}$  is simply  $\Delta H^\circ$  for the system.

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

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**The total entropy of the universe increases in any spontaneous process.**

*Entropy increases with the freedom of motion of molecules.*

Therefore,  **$S(g) > S(l) > S(s)$**

In general,  **$\Delta S$  is positive** in a chemical reaction, if

- liquids or solutions formed from solids
- Gases formed from solids or liquids
- number of gas molecule increased during reaction

➤ Entropy increases ( $\Delta S > 0$ ) when a solid melts to the liquid. *Crystalline solids have proper orientation. Molecules in liquid are less ordered.*

➤ Entropy increases ( $\Delta S > 0$ ) when a liquid evaporates to the gas.

➤ Entropy increases ( $\Delta S > 0$ ) when a solute is dissolved in a solvent.

*Solution is more random than separate solute and solvent*

The number of ways a system can be arranged is the number of microstates it has. The entropy of a system is given by

$$S = k \ln W$$

where  $W$  is the number of possible microstates, and  $k$  is Boltzmann's constant =  $1.38 \times 10^{-23} \text{ J/K}$ .

Entropy increases with temperature, since the particles vibrate and move about more rapidly, and so there is greater disorder. It also increases with increasing volume, as with an expanding gas, and with the number of independently moving particles. Thus, entropy increases solid < liquid < gas.

For reversible processes:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

For irreversible processes:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

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Molecules exhibit several types of motion (Kinetic energies):

- Translational: Movement of a molecule from one place to another.
- Vibrational: Periodic motion of atoms within a molecule.
- Rotational: Rotation of the molecule on about an axis or rotation about  $\sigma$  bonds.



## PRINCIPAL MODES OF VIBRATION

### ➤ $3N-6$ possible normal modes of vibration

$N$  = number of atoms in a molecule; Degrees of freedom =  $3N$

Degrees of freedom	linear	non-linear
Translational	3	3
Rotational	2	3
Vibrational	$3N-5$	$3N-6$
Total	$3N$	$3N$

$N$  = number of atoms in molecule

### **H<sub>2</sub>O for example**

- 3 atoms; - Degrees of freedom =  $3 \times 3 = 9$
- Normal modes of vibration =  $9-6 = 3$

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- The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process. (**Clausius**)
- "It is impossible in any way to diminish the entropy of a system of bodies without there by leaving behind changes in other bodies" (**Planck**)
- "In any irreversible process the total entropy of all bodies concerned is increased." (**Lewis**)

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

Equilibrium process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

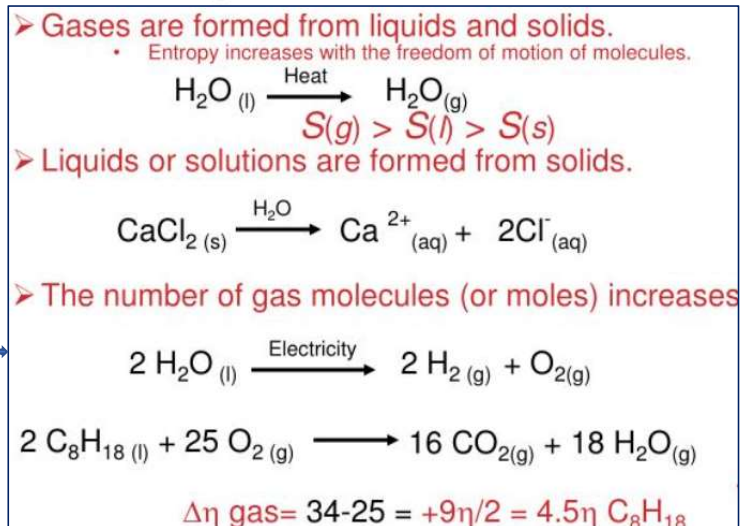
The number of microstates (W) and, therefore, the entropy (S) tends to increase with increase in

➤ Temperature (T)

➤ Volume (V)

➤ The number of independently moving molecules ( $\eta$ )

1. **Entropy** is a thermodynamic property that measures the degree of randomization or disorder at the **microscopic level**. The natural state of affairs is for **entropy to be produced** by all processes.
2. A **macroscopic** feature which is associated with entropy production is a loss of ability to do useful work. Energy is degraded to a less useful form, and it is sometimes said that there is a decrease in the **availability** of energy.
3. Entropy is an extensive thermodynamic property. In other words, the entropy of a complex system is the sum of the entropies of its parts.
4. The notion that **entropy can be produced, but never destroyed**, is the **second law of thermodynamics**.



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Clausius discovered the state function  $S$  in 1854 and called it the transformation content. Later, he renamed it entropy, from the Greek word trope, meaning “transformation,” since  $S$  is related to the transformation of heat to work. **The Helmholtz and Gibbs energies**

Consider a system in thermal equilibrium with its surroundings at a temperature  $T$ . When a change in the system occurs, there is a transfer of energy as heat between the system and the surroundings, the Clausius inequality becomes

$$dS - \frac{dq}{T} \geq 0$$

When energy is transferred as heat at constant pressure, and there is no work other than expansion work, we can write  $dq_p = dH$  and get  $TdS \geq dH$  (constant  $p$ , no additional work)

At either constant enthalpy or constant entropy this inequality respectively becomes  $dS_{H,p} \geq 0$   $dH_{S,p} \leq 0$

Since these eqns have the forms  $dU - TdS \leq 0$  and  $dH - TdS \leq 0$ , respectively, they can be expressed just by introducing two more thermodynamic quantities.

One is the **Helmholtz energy**,  $A$ , and the other is the **Gibbs energy**,  $G$

- Predicts the direction of a spontaneous reaction.
- Uses properties of the system to calculate.
- For a constant pressure-temperature process:  $\Delta G_T = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$

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The condition for material equilibrium in a closed system capable of doing only P-V work and held at **constant T and V** is minimization of the system's state function  $U - TS$ . This state function is called the Helmholtz free energy, the Helmholtz energy, the Helmholtz function, or the work function and is symbolized by A:  $A = U - TS$

Thus, the state function  $H - TS$  continually decreases during material changes at **constant T and P** until equilibrium is reached. The condition for material equilibrium at constant T and P in a closed system doing P-V work only is minimization of the system's state function  $H - TS$ . This state function is called the Gibbs function, the Gibbs energy, or the Gibbs free energy and is symbolized by G:  $G = H - TS = (U + PV) - TS$

When the state of the system changes at constant temperature, the two properties change as follows: (a)  $dA = dU - TdS$  (b)  $dG = dH - TdS$

Therefore, for a material change at constant T and P in a closed system in mechanical and thermal equilibrium and capable of doing only P-V work,  $dG, d(H - TS) \leq 0$  const. T, P where the equality sign holds at material equilibrium.

$$dH = d(U + PV) = dU + d(PV) = dU + P dV + V dP$$

$$= (T dS - P dV) + P dV + V dP$$

$$dH = T dS + V dP$$

$$dG = d(H - TS) = dH - T dS - S dT = T dS + V dP - T dS - S dT$$

$$= -S dT + V dP$$

**Standard free energy of formation ( $\Delta G^\circ$ )** is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

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In a closed system capable of doing only P-V work, the constant T and V material equilibrium condition is the minimization of the Helmholtz energy A, and the constant T and P material equilibrium condition is the minimization of the Gibbs energy G:  $dA = 0$  at equil., const. T, V       $dG = 0$  at equil., const. T, P where dA: infinitesimal change in A due to an infinitesimal amount of chemical reaction or phase change at constant T and V, dG: infinitesimal change in G due to an infinitesimal amount of chemical reaction or phase change at constant T and P. G can be expressed as function of T, P, and the  $n_i$ 's (mole numbers of i components of the one-phase system)

$$G = G(T, P, n_1, \dots, n_i) \quad \text{eqn. (2)}$$

For a reversible process with no change in composition,  $dG = -Sdt + VdP$ , rev. proc., only P-V work,  $n_i$  fixed

We define the chemical potential  $\mu_i$  of substance i in the one-phase system as

$$\mu_i = (\delta G / \delta n_i)_{T, P, n} \quad \text{one-phase system, thermal \& mech. equil., only P-V work}$$

where G is the Gibbs energy of the one-phase system. Total differential of eqn. (2) then becomes

$$dG = -Sdt + VdP + \sum \mu_i dn_i$$

**This equation is the key equation of chemical thermodynamics.** The molar Gibbs energy or chemical potential  $\mu$  is the potential of a substance to undergo chemical change. At equilibrium, the chemical potential of a substance is the same throughout a sample, irrespective of how many phases are present.

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$$\Delta S_{\text{univ}} = \Delta S_{\text{syst or rxn}} + \Delta S_{\text{surr}}$$

• Since:  $\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$

• Then:

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \frac{-\Delta H_{\text{system}}}{T}$$

Multiplying both sides by  $-T$ ,

$$-T\Delta S_{\text{univ}} = -T\Delta S_{\text{syst}} + \Delta H_{\text{syst}}$$

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{syst}} - T\Delta S_{\text{syst}}$$

$-T\Delta S_{\text{univ}}$  is defined as the  
**Gibbs (free) Energy,  $\Delta G$ .**

$$\Delta G_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

When  $\Delta S$  is positive,  $\Delta G$  is negative.

When  $\Delta G$  is negative, the process is spontaneous.

At temperatures other than  $25^\circ \text{C}$ ,

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

There are two parts to the free energy equation: completely reversible process.

- $\Delta H^\circ$  — the enthalpy term
- $T\Delta S^\circ$  — the entropy term

The temperature dependence of free energy, then comes from the entropy term.

**Gibbs Energy** ( $-T\Delta S$ ) measures the "useful" or process-initiating work obtainable from an isothermal, isobaric thermodynamic system. Technically, the Gibbs free energy is the *maximum* amount of non-expansion work which can be extracted from a closed system or this maximum can be attained only in a

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$\Delta H$	$\Delta S$	$\Delta G$	Example
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$
+	-	$\Delta G$ is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
-	+	$\Delta G$ is always negative. Reaction proceeds spontaneously at all temperatures.	$2\text{H}_2\text{O}_2(l) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
-	-	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$

	$\Delta G =$	$\Delta H$	$\Delta S$	$-T\Delta S$	
$2\text{O}_3(g) \longrightarrow 3\text{O}_2(g)$		-			Spontaneous @ all T
$3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$		+			NonSpontaneous @ all T
$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$		-			Spontaneous @ low T
$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$		+			Spontaneous @ high T

$K$	$\ln K$	$\Delta G^\circ$	Comments
$> 1$	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
$< 1$	Negative	Positive	Reactants are favored over products at equilibrium.

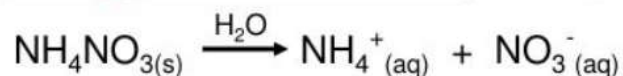
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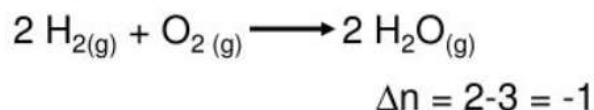
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### { Entropy Driven Reactions }



### { Enthalpy Driven Reaction }



### { Entropy & Enthalpy Driven Reaction }



Enthalpy  
 $\Delta H = +$

$\Delta H = -$

$\Delta H = -$

Entropy  
 $\Delta S = +$   
( $-T\Delta S$ )

$\Delta S = -$   
( $+T\Delta S$ )

$\Delta S = +$   
( $-T\Delta S$ )



$$\Delta G^\circ_{\text{rxn}} = \sum n \Delta G^\circ_{f(\text{prod})} - \sum m \Delta G^\circ_{f(\text{react})}$$

$$[12 \text{CO}_{2(\text{g})} + 6 \text{H}_2\text{O}_{(\text{g})}] - [2 \text{C}_6\text{H}_6(\text{l}) + 15 \text{O}_{2(\text{g})}]$$

$$[12(-394) + 6(-229)] - [2(125) + 15(0)]$$

$$\Delta G^\circ_{\text{rxn}} = -6352 \text{ J/mol} \cdot \text{K}$$

Standard Molar Gibbs Energy of Formation ( $\Delta G^\circ_f$ )	
$\text{CO}_{2(\text{g})}$	-394
$\text{H}_2\text{O}_{(\text{g})}$	-229
$\text{C}_6\text{H}_6(\text{l})$	125

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

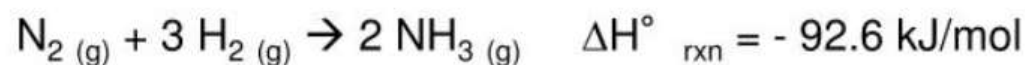
where  $n$  and  $m$  are the stoichiometric coefficients.

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Calculate the  $\Delta S_{\text{univ}}$  for the synthesis of ammonia @ 25°C.



$$\Delta S_{\text{univ}} = \Delta S_{\text{syst or rxn}} + \Delta S_{\text{surr}}$$

$$\Sigma n \Delta S_{(\text{prod})} - \Sigma m \Delta S_{(\text{react})}$$

$$2(192.5) - [(191.5) + 3(130.6)]$$

$$\Delta S^\circ_{\text{syst}} = -199 \text{ J/K}\cdot\text{mol}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$= \frac{-(-92.6 \text{ kJ/mol} \times 1000 \text{ J/kJ})}{298 \text{ K}}$$

$$\Delta S_{\text{surr}} = 311 \text{ J/K}\cdot\text{mol}$$

$$\Delta S_{\text{univ}} = -198.3 \text{ J/K}\cdot\text{mol} + 311 \text{ J/K}\cdot\text{mol}$$

$$\Delta S_{\text{univ}} = 113 \text{ J/K}\cdot\text{mol}$$

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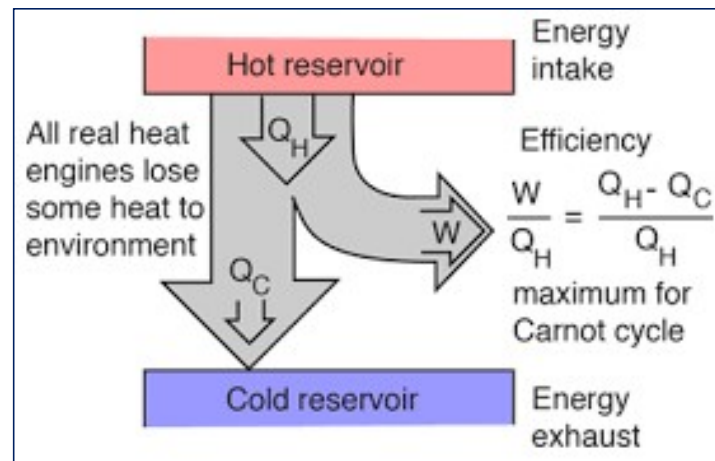
## Heat Engine

A heat engine is an energy transformation device. It is a device that converts some of the random molecular energy of heat into macroscopic mechanical energy (work). Therefore, from 2<sup>nd</sup> law, the thermal efficiency of a heat engine can never be 100%. Energy transformation efficiency or thermal efficiency of heat engine [ $\eta$ : eta] is defined as the ratio of net work output to the total heat input.

$\eta = \text{Net work output} / \text{Heat input}$

$$= W_{\text{net}} / Q_{\text{in}}$$

$$= Q_{\text{in}} - Q_{\text{out}} / Q_{\text{in}} \quad [\eta \text{ always} < 1 \text{ \& never} > 60\text{-}70\% \text{ in actual practice}]$$



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### Carnot's Principle

*The second law is used to prove Carnot's principle: No heat engine can be more efficient than a reversible heat engine when both engines work between the same pair of temperatures  $\tau_H$  and  $\tau_C$ . Equivalently, the maximum amount of work from a given supply of heat is obtained with a reversible engine.*

*To prove Carnot's principle, we assume it to be Carnot cycle: is a hypothetical cycle. This is the most efficient and ideal reversible cycle, first proposed by the French engineer Nicolas Sadi Carnot in 1824. The heat engine operating on this cycle is known as Carnot engine. It is not possible to construct a Carnot engine, as it consists solely of reversible processes in all stages. Carnot cycle consists of four successive operational steps:*

- 1. Reversible isothermal expansion*
- 2. Reversible adiabatic expansion*
- 3. Reversible isothermal compression*
- 4. Reversible adiabatic compression*

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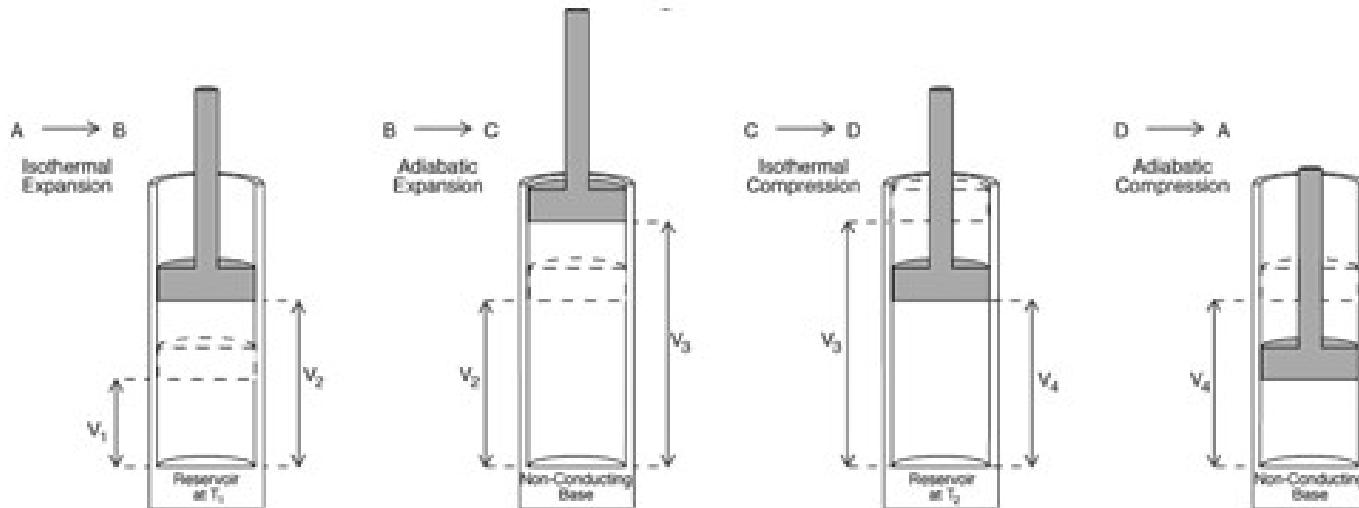
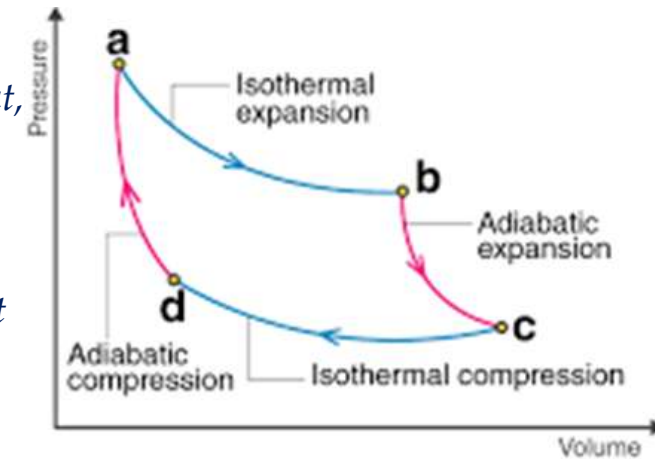
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1. **Reversible isothermal expansion** from A to B at  $T_h$ ; the entropy change is  $q_h / T_h$ , where  $q_h$  is the energy supplied to the system as heat from the hot source.

2. **Reversible adiabatic expansion** from B to C. No energy leaves the system as heat, so the change in **entropy is zero**. In the course of this expansion, the temperature falls from  $T_h$  to  $T_c$ , the temperature of the cold sink.

3. **Reversible isothermal compression** from C to D at  $T_c$ . Energy is released as heat to the cold sink; change in entropy of the system is  $q_c / T_c$ ; in this expression  $q_c$  is -ve.

4. **Reversible adiabatic compression** from D to A. No energy enters the system as heat, so the change in **entropy is zero**. The temperature rises from  $T_c$  to  $T_h$ .



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We now calculate the Carnot-cycle efficiency  $e_{\text{rev}}$  on the ideal-gas temperature scale  $T$ . We use a perfect gas as the working substance and restrict ourselves to  $P$ - $V$  work. The first law gives  $dU = dq - P dV$  for a reversible volume change.

For a perfect gas,  $P = nRT/V$  and  $dU = C_v(T) dT$ . The first law becomes

$$C_v T dT = dq - nRT dV/V$$

for a perfect gas. Dividing by  $T$  and integrating over the Carnot cycle, we get

$$\oint C_v(T) \frac{dT}{T} = \oint \frac{dq}{T} - nR \oint \frac{dV}{V}$$

Each integral is the sum of four line integrals,

$$\oint C_v(T) \frac{dT}{T} = \int_{T_1}^{T_2} \frac{C_v(T)}{T} dT + \int_{T_2}^{T_3} \frac{C_v(T)}{T} dT + \int_{T_3}^{T_4} \frac{C_v(T)}{T} dT + \int_{T_4}^{T_1} \frac{C_v(T)}{T} dT$$

Which becomes 
$$\oint C_v(T) \frac{dT}{T} = 0$$

$$\oint \frac{dq}{T} = \frac{q_H}{T_H} + \frac{q_C}{T_C} = 0$$

$$e_{\text{rev}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}$$

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We learned that even some of the **endothermic** processes are spontaneous if the process proceeds with **increase in entropy** ( $\Delta S$  positive).

However, some processes occur spontaneously with **decrease in entropy**. And most of them are **highly exothermic processes** ( $\Delta H$  negative)

Thus, the spontaneity of a reaction seems to relate both thermodynamic quantity namely Enthalpy and Entropy.

**Gibbs related both H and S.**

He defined a term called '**free energy**', G

$$G = H - TS$$

<b>Spontaneous</b>	$\Delta S_{\text{universe}} > 0$	$\Delta G < 0$
<b>Non-spontaneous</b>	$\Delta S_{\text{universe}} < 0$	$\Delta G > 0$
<b>Equilibrium</b>	$\Delta S_{\text{universe}} = 0$	$\Delta G = 0$

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$\Delta G^\circ$  (at 1 atm) generally used to decide if a reaction is spontaneous (Yes, if negative)

### Three ways to obtain $\Delta G^\circ$ for a reaction

#### (a) from $\Delta H^\circ$ and $\Delta S^\circ$

requires  $\Delta H_f^\circ$  and  $S^\circ$  data for all reactants and products

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

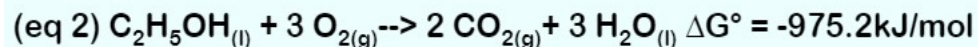
$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

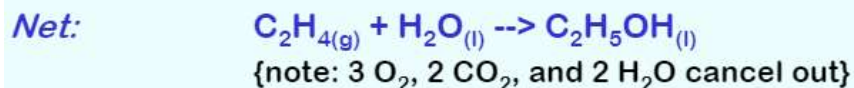
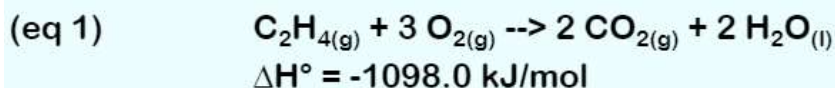
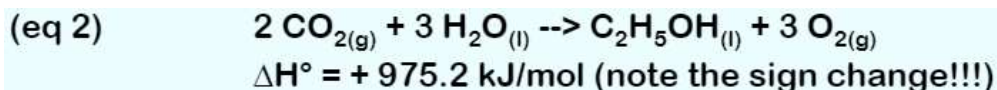
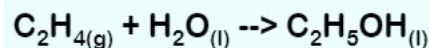
If reaction is reversed, change sign of  $\Delta G^\circ$ .

If reaction is multiplied or divided by a factor, apply same factor to  $\Delta G^\circ$ .

$\Delta G^\circ$  for overall reaction = sum of  $\Delta G^\circ$  values for individual reactions.



Calculate  $\Delta G^\circ$  for the following reaction:



$$\Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ = 975.2 + (-1098.0) = -122.8 \text{ kJ/mol}$$

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(a) Effect of Temperature on  $\Delta G$

$\Delta G$  depends on  $\Delta H$  and  $\Delta S$ :  $\Delta G = \Delta H - T\Delta S$

but  $\Delta H$  and  $\Delta S$  are relatively independent of temperature, so

$\Delta G$  at some temperature  $T$  can be estimated.

$$\Delta G^\circ_T \approx \Delta H^\circ_{298} - T\Delta S^\circ_{298}$$

(b) for a system at equilibrium:

$$G_{\text{products}} = G_{\text{reactants}} \quad \text{and} \quad \Delta G = 0$$

$$\text{since } \Delta G = \Delta H - T\Delta S = 0$$

$$\Delta H = T\Delta S \quad \text{or} \quad T = \Delta H / \Delta S$$

(c) Relationship between  $\Delta G^\circ$  and Equilibrium Constant ( $K$ )

For any chemical system:

$$\Delta G = \Delta G^\circ + (RT) \ln Q$$

If  $\Delta G$  is not zero, then the system is not at equilibrium. It will spontaneously shift toward the equilibrium state.

At Equilibrium:  $\Delta G = 0$  and  $Q = K$

$$\therefore \Delta G^\circ = -RT \ln K$$

for gaseous reactions:  $K = K_p$

for solution reactions:  $K = K_c$

{units of  $\Delta G$  must match those of  $R$  value}

Temperature helps determine whether  $\Delta G$  will be negative, and the process spontaneous.

$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G (= \Delta H - T\Delta S)$
-	+	-	- (spontaneous)
+	-	+	+ (non-spontaneous)
-	-	+	+ or - depends on $T$
+	+	-	+ or - depends on $T$

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

↑  
increase in  
entropy of  
surroundings

↑  
increase in  
entropy of  
system

$-\Delta G$  is in fact the increase in entropy in the universe.



Is the reaction spontaneous? **Yes**

What is the sign of  $\Delta G$ ?  **$\Delta G = \text{negative}$**

What is the sign of  $\Delta H$ ?  **$\Delta H = \text{negative (exothermic!)}$**

What is the sign of  $\Delta S$ ?  **$\Delta S = \text{positive}$**

$$\Delta G^\circ = -RT \ln K$$

$K$  values can be determined from thermodynamic data

when  $K > 1$   $\Delta G^\circ$  is negative

$\therefore$  spontaneous reactions have

large  $K$  and negative  $\Delta G^\circ$  values

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### Third Law of Thermodynamics

Third law of thermodynamics concerns the entropy of perfectly-ordered crystals at zero kelvin.

**Third law of thermodynamics or the Nernst heat theorem:** states that the absolute entropy of a pure crystalline substance is zero at absolute zero temperature.

The entropy (S) of a pure crystalline substance at absolute zero (-273° C) is 0

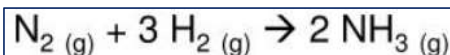
When a chemical reaction or phase transition is studied at low temperatures, and all substances are pure crystals presumed to be perfectly ordered, the entropy change is found to approach zero as the temperature approaches zero kelvin:

$$\lim \Delta S = 0 \text{ (pure, perfectly-ordered crystal)}$$

$$\Delta S_{298}^{\circ} = \sum n S_{\text{products}}^{\circ} - \sum m S_{\text{reactants}}^{\circ}$$

$T \rightarrow 0$

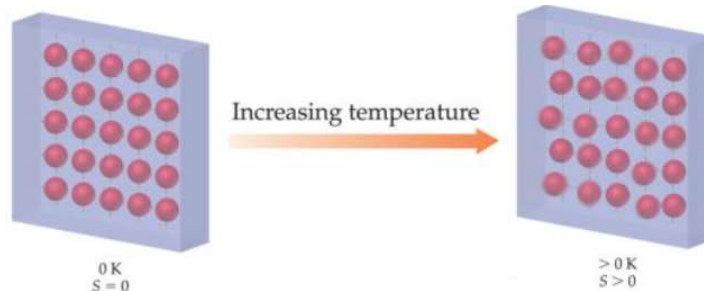
where  $n$  and  $m$  are the coefficients in the balanced chemical equation



$$\Delta S^{\circ} = \sum n \Delta S^{\circ}_{\text{(prod)}} - \sum m \Delta S^{\circ}_{\text{(react)}}$$

$$2(192.5) - [(191.5) + 3(130.6)]$$

$$\Delta S^{\circ} = -198.3 \text{ J/K}$$



Gases	$S^{\circ}, \text{J/mol-K}$
H <sub>2</sub> (g)	130.6
N <sub>2</sub> (g)	191.5
O <sub>2</sub> (g)	205.0
H <sub>2</sub> O(g)	188.8
NH <sub>3</sub> (g)	192.5
CH <sub>3</sub> OH(g)	237.6
C <sub>6</sub> H <sub>6</sub> (g)	269.2
<b>Liquids</b>	
H <sub>2</sub> O(l)	69.9
CH <sub>3</sub> OH(l)	126.8
C <sub>6</sub> H <sub>6</sub> (l)	172.8
<b>Solids</b>	
Li(s)	29.1
Na(s)	51.4
K(s)	64.7
Fe(s)	27.23
FeCl <sub>3</sub> (s)	142.3
NaCl(s)	72.3

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*This is true only for changes involving substances in internal equilibrium. It does not hold for a transition involving a supercooled liquid, which is not in internal equilibrium.*

*The Nernst–Simon statement of the third law of thermodynamics:*

*For any isothermal process that involves only substances in internal equilibrium, the entropy change goes to zero as  $T$  goes to zero:*

$$\lim_{T \rightarrow 0} \Delta S = 0 (\text{pure, perfectly-ordered crystals/mixtures})$$

$T \rightarrow 0$

Unlike  $\Delta H_f^\circ$ , the  $S^\circ$  is **NOT** zero for pure elements in their standard state.

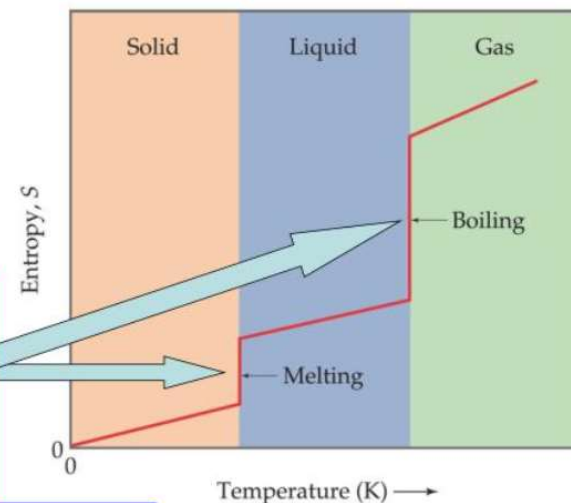
As expected,  $S^\circ$  for gases is greater than liquids and solids.

$S^\circ$  increases as the molar mass increases.

As the number of atoms in a molecule increases,  $S^\circ$  also increases. (see below)

Note the vertical jump in entropy corresponding to phase changes.

$$S(g) > S(l) > S(s)$$



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## Summary

- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$  (For spontaneous process)
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$  (For non-spontaneous process)
- $\Delta S^\circ = \sum n S^\circ(\text{products}) - \sum m S^\circ(\text{reactants})$
- For an isothermal process and at constant P,  
$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$
$$\Delta S_{\text{surr}} = \frac{-\Delta H^\circ_{\text{rxn}}}{T}$$
- $\Delta H^\circ_{\text{rxn}} = \sum n H_f^\circ(\text{products}) - \sum m H_f^\circ(\text{reactants})$
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G^\circ_{\text{rxn}} = \sum n G_f^\circ(\text{products}) - \sum m G_f^\circ(\text{reactants})$
- $\Delta G = \Delta G^\circ + RT \ln Q$
- $\Delta G^\circ = -RT \ln K$

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### **Chemical equilibrium:**

Chemical reactions move towards a dynamic equilibrium where both reactants and products are present but have no further tendency to undergo further change. Thermodynamics can be used to predict the equilibrium composition under any reaction condition.

**The reaction Gibbs energy:** For the equilibrium  $A \rightleftharpoons B$ , the quantity  $\xi$  (xi) is called the **extent of reaction**; it has the dimensions of amount of substance and is in moles. Change in the amount of A present is  $dn_A = -d\xi$  and the change in the amount of B present is  $dn_B = +d\xi$ . If initially 2.0 mol A is present and we wait until  $\Delta\xi = +1.5$  mol, then the amount of A remaining will be 0.5 mol.

The **reaction Gibbs energy**,  $\Delta_r G$ , is defined as the slope of the graph of the Gibbs energy plotted against the extent of reaction:

$$\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{p,T}$$

$\Delta_r$  signifies a derivative, the slope of  $G$  with respect to  $\xi$ . The corresponding change in Gibbs energy is

$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi$$

This equation can be reoriented as  $\left( \frac{\partial G}{\partial \xi} \right)_{p,T} = \mu_B - \mu_A$

or

$$\Delta_r G = \mu_B - \mu_A$$

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$\Delta_r G$  can also be interpreted as the difference between the chemical potentials (the partial molar Gibbs energies) of the reactants and products at the composition of the reaction mixture.

The reaction  $A \rightarrow B$  is spontaneous when  $\mu_A > \mu_B$ , whereas the reverse reaction is spontaneous when  $\mu_B > \mu_A$ . The slope is zero, and the reaction is spontaneous in neither direction, when  $\mu_B = \mu_A$  or  $\Delta_r G = 0$ , composition of reaction mixture at equilibrium.

### Exergonic and endergonic reactions

The spontaneity of a reaction at constant temperature and pressure can be expressed in terms of the reaction Gibbs energy:

- If  $\Delta_r G < 0$ , forward reaction is spontaneous/exergonic (work-producing)  
e.g. pair of weights joined by a string
- If  $\Delta_r G > 0$ , the reverse reaction is spontaneous, called endergonic (work-consuming),  
e.g. electrolysis of water
- If  $\Delta_r G = 0$ , the reaction is at equilibrium.

When A and B are perfect gases

$$\Delta_r G = \mu_B - \mu_A = (\mu_B^\ominus + RT \ln p_B) - (\mu_A^\ominus + RT \ln p_A)$$

$$= \Delta_r G^\ominus + RT \ln \frac{p_B}{p_A} = \Delta_r G^\ominus + RT \ln Q \quad Q = \frac{p_B}{p_A}$$

$Q$  is an example of a **reaction quotient**. It ranges from 0 to  $p_B = 0$ ,  $p$ : pressure. The standard **reaction Gibbs energy**,  $\Delta_r G^\ominus$ , is defined as the difference in the standard molar Gibbs energies of the reactants and products.

$$\Delta_r G^\ominus = G_{B,m}^\ominus - G_{A,m}^\ominus = \mu_B^\ominus - \mu_A^\ominus$$

At equilibrium  $\Delta_r G = 0$ . The ratio of partial pressures at equilibrium is denoted  $K$

$$0 = \Delta_r G^\ominus + RT \ln K$$

$$\text{or} \quad RT \ln K = -\Delta_r G^\ominus$$

$$K = e^{-\Delta_r G^\ominus / RT}$$

$$K = \left( \frac{p_B}{p_A} \right)_{\text{equilibrium}}$$

- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above 0°C it is spontaneous for ice to melt.
- Below 0°C the reverse process is spontaneous.

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**1. Thermodynamics:** Energy differences and transfers between systems.

**2. Systems:**

- **Isolated system:** "have walls or boundaries that are rigid, do not permit transfer of mechanical energy, perfectly insulating, and impermeable. They have a constant energy and mass content.

- **Adiabatic systems:** Perfectly insulated systems.

- **Closed systems:** have walls that allow transfer of energy in or out of the system but are impervious to matter. They contain a fixed mass and composition, but variable energy.

- **Open Systems:** have walls that allow transfer of both energy and matter to and from the system.

**3. Equilibrium:** "A system at equilibrium has none of its properties changing with time". A system at equilibrium will return to that state after being disturbed.

**4. State Variables:** Variables that define the state of a system.

- **Extensive variables are proportional** to the quantity of matter being considered (V, total Cp).

- **Intensive variables are** independent of quantity (concentration, viscosity, density, molar Cp)

**11. ZEROth LAW:** "Two bodies in thermal equilibrium with a third are in thermal equilibrium with each other" (Basis of the concept of temperature)

**12. FIRST LAW:** "The algebraic sum of all energy changes in an isolated system is zero" (Conservation of energy). Energy can be converted from one form to another but cannot be created or destroyed.  $\Delta U = q + w$ . *This is based only on observation*

**13. SECOND LAW:** "Spontaneous changes are those which, if carried out under the proper conditions, can be made to do work. If carried out reversibly they yield a maximum amount of work. In natural processes, maximum work is never obtained.

**14. THIRD LAW:**

- First expressed as Nernst's Heat Theorem: "Nernst (1905): As  $T \rightarrow 0$  K,  $\Delta S \rightarrow 0$  for all isothermal processes in condensed phases"

- More general and useful formulation by M. Planck: "Planck (1911): As  $T \rightarrow 0$  K,  $S \rightarrow 0$  for every chemically homogeneous substance in a perfect crystalline state"

- This leads to the following interesting corollary: "It is impossible to decrease the temperature of any system to  $T = 0$  K in a finite number of steps"

**5. Work (w):** "The transfer of energy from one mechanical system to another. It is always completely convertible to the lifting of a weight". "The energy that flows across a system boundary in response to a force moving through a distance (such as happens when a system changes volume)".

**6. Heat (q):**

- "The transfer of energy that results from temperature differences".

- "The energy that flows across a system boundary in response to a temperature gradient."

- "That part of any energy transfer that is not accounted for by mechanical work ( $F \times D$ )."

- $q = \Delta U - w$

**7. Heat Capacity:** The relation between heat transferred to a body and the change in T.

**8. Enthalpy:** The increase in enthalpy of a system is equal to the heat absorbed at constant pressure, assuming the system does only PV work.

**9. Entropy:** A measure of the loss of capacity of the system to do work.

**10. Gibbs free energy** is a measure of the potential for reversible or maximum work that may be done by a system at constant temperature and pressure. It is a thermodynamic property that was defined in 1876 by Josiah Willard Gibbs to predict whether a process will occur spontaneously at constant temperature and pressure.

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