

Class XI Chemistry

Unit 6

THERMODYNAMICS

Topic:-THERMODYNAMIC TERMS

- Sub topics:-
 - The System and the Surroundings
 - Types of the System
 - State of the System
 - State Functions
 - Adiabatic System

By Vijay Kumar Sethi

Thermodynamics

- The branch of science which deals with the quantitative relationship between heat and other forms of energies is called thermodynamics
- For example,
 - Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air.
 - The chemical energy used to do mechanical work when a fuel burns in an engine
 - The chemical energy used to provide electrical energy through a galvanic cell like dry cell.
- The study of these energy transformations forms the subject matter of thermodynamics

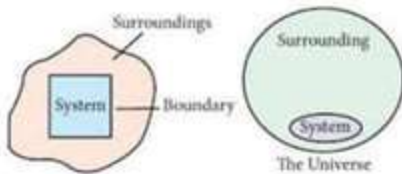
The System and the Surroundings

- The part of universe in which observations are made or which is under investigation is called **system**
- Surroundings is the part of universe other than system . The **surroundings** include everything other than the system.
- System and the surroundings together constitute the universe .
- The universe = The system + The surroundings

Continue...

The System and the Surroundings

- For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings
- System and surroundings are separated by a boundary.
- This boundary may be real or imaginary.



Types of the System

Open System

- There is **exchange of energy and matter** between system and surroundings.
- For example, the presence of reactants in an open beaker.
- Here the boundary is an imaginary

Closed System

- There is **no exchange of matter**, but **exchange of energy** is possible between system and the surroundings.
- For example, the presence of reactants in a closed vessel made of conducting material.

Isolated System

- There is **no exchange of energy and matter** between the system and the surroundings
- For example, the presence of reactants in a thermos flask or any other closed insulated vessel

Continue...

Types of the System



(a) Open System



(b) Closed System



(c) Isolated System



saucepan without lid
Open system



saucepan with lid
Closed system



Isolated system

The State of the System

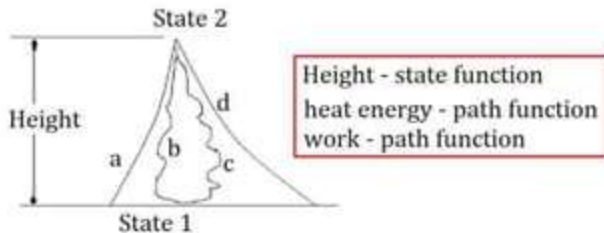
- The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties.
- We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc.

State of System

- It is the *condition of system* which is described in terms of certain measurable properties such as temperature(T), pressure(P), volume(V) etc. of the system.

State Functions

- The macroscopic properties whose values depend only on the state of the system (initial and final) and not on how it is reached are called state functions.
- For example, P , T , V , Internal energy, Enthalpy, Entropy



- **Path functions** depend on the **path** taken to reach one state from another.

Adiabatic System

- The system which will **not allow exchange of heat** between the system and surroundings through its boundary but energy of the system may change by work.
- Adiabatic process** is a process in which there is no transfer of heat between the system and surroundings.
- The wall separating the system and the surroundings is called the **adiabatic wall**.
- It happens so fast, there is not enough time to exchange heat with surroundings



Fig. An adiabatic system which does not permit the transfer of heat through its boundary.

Adiabatic System	Isolated System
It has no exchange of energy and matter with the surrounding environment	It has no transfer of energy and matter through its boundaries .
It has a surrounding environment	It doesn't have a surrounding environment
It does not gain or loss energy but internal energy can be changed due to work done by the system	Energy is conserved
Internal energy can be changed	Internal energy can not be changed

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THERMODYNAMICS

- Topic:-
 - Internal Energy (U)
 - Mathematical statement of the first law of thermodynamics

By Vijay Kumar Sethi

Internal Energy (U)

- Total energy of the system is called internal energy of the system.
- It is the sum of kinetic(translational , vibrational and rotational) potential , chemical, electrical, mechanical energies etc.
- Internal energy is a state function-depends on initial and final states of the system
- Absolute value of U can not be determined.
- Change in internal energy (ΔU) is determined. $\Delta U = U_2 - U_1$
- It may change, when
 - heat passes into or out of the system,
 - work is done on or by the system,
 - matter enters or leaves the system.

Ways of Changing Internal Energy

Work: Consider an adiabatic system

- Initial state of the system = A and its temperature = T_A .
- Internal energy of the system in state A = U_A .
- We can change the state of the system in two different ways.

One way: By mechanical work (1 kJ):- by rotating a set of small paddles

- Final State = B state and its temperature = T_B .
- if $T_B > T_A$ and the change in temperature, $\Delta T = T_B - T_A$.
- The internal energy of the system in state B = U_B and
- The change in internal energy, $\Delta U = U_B - U_A = W_{ad}$.

Continue...

Ways of Changing Internal Energy Work

- **Second way:** We now do an equal amount (i.e., 1kJ) electrical work with the help of an immersion rod and note down the temperature change.
- We find that the change in temperature is same as in the earlier case, $T_B - T_A$
- The change in internal energy, $\Delta U = U_B - U_A = W_{ad}$.
- Therefore, internal energy, U , of the system is a state function.
- **J. P. Joule** showed that a given amount of work done on the system, no matter how it was done (irrespective of path) produced the same change of state, as measured by the change in the temperature of the system. **By conventions:-**
- Work done **on** the system = positive work **(+W)** internal energy of system increases.
- Work done **by** the system = negative work **(-W)** internal energy of the system decreases.

Continue...

Ways of Changing Internal Energy

Heat(q) :

- If system and surroundings are at different temperatures , internal energy of the system is changed by transfer of heat through thermally conducting walls
- If temperature of System = T_A and Temperature of surroundings = T_B
- $T_B < T_A$ heat is transferred from system to surroundings till $T_B = T_A$
- $T_B > T_A$ heat is transferred from surroundings to system till $T_B = T_A$
- In this case change in internal energy, $\Delta U = q$, when no work is done at constant volume.



Fig. A system which allows heat transfer through its boundary.

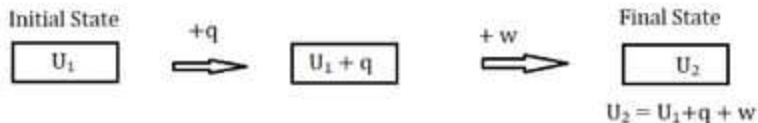
Continue...

Ways of Changing Internal Energy

Heat(q) :

- **By conventions**
- *The q is positive ($+q$)= heat is transferred from the surroundings to the system and the internal energy of the system increases and*
- *q is negative ($-q$) = heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system..*

Mathematical statement of the first law of thermodynamics



- $\Delta U = U_2 - U_1 = q + w$
- $\Delta U = q + w$ mathematical statement of the first law of thermodynamics,
- which states that *The energy of an isolated system is constant.*
- It is commonly stated as the law of conservation of energy i.e., energy can neither be created nor be destroyed.

Continue...

Mathematical statement of the first law of thermodynamics

- q and w are path functions but $q + w = \Delta U$ will depend only on initial and final state therefore $(q + w)$ is state function
- It will be independent of the way the change is carried out.
- If there is no transfer of energy as heat or as work (isolated system) i.e., if $w = 0$ and $q = 0$, then $\Delta U = 0$.

Problem 6.1

Express the change in internal energy of a system when

- (i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?

Solution:- $\Delta U = w_{ad}$, wall is adiabatic

- (ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?

Solution:- $\Delta U = -q$, thermally conducting walls

- (iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

Solution:- $\Delta U = q - w$, closed system.

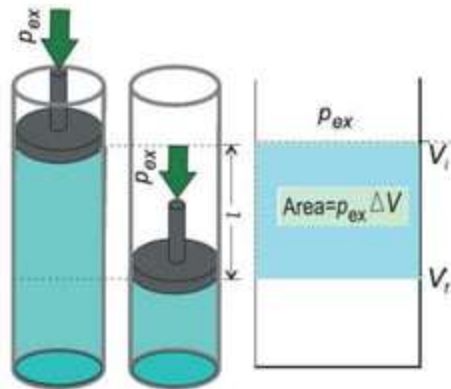
Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - Pressure-Volume Work
 - Reversible and Irreversible process

By Vijay Kumar Sethi

Pressure-Volume Work

- A cylinder contains one mole of an ideal gas fitted with a frictionless piston.
- Initial volume the gas is V_i and pressure of the gas inside is p .
- p_{ex} = external pressure , $p_{ex} > p$
- piston is moved inward till $p_{ex} = p$
- Final volume = V_f .
- During this compression, piston moves a distance, l and its cross-sectional area of the piston is A



Pressure-Volume Work

then, volume change = $l \times A = \Delta V = (V_f - V_i)$

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

Therefore, force on the piston = $p_{\text{ex}} \cdot A$

If w is the work done on the system by movement of the piston then

$$w = \text{force} \times \text{distance} = p_{\text{ex}} \cdot A \cdot l$$

$$w = p_{\text{ex}} \cdot (V_f - V_i) = -p_{\text{ex}} \Delta V$$

$$w = -p \Delta V$$

- The negative sign of this expression is required to obtain conventional sign for w , which will be positive.
- **compression work** is done on the system.
- $(V_f - V_i)$ will be negative and negative multiplied by negative will be positive.
- This formula is also applicable for **expansion work** which is done by the system so it will be negative.
- In expansion $(V_f - V_i)$ will be positive

Reversible process

- A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal (इन्फिनिटिसिमल् extremely small)change.
- A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other.

Irreversible processes

- Processes other than reversible processes are known as irreversible processes.
- All natural processes are irreversible.

Differences between Reversible and Irreversible process

Reversible process	Irreversible process
The process is carried out infinitesimally slowly.	It is carried out rapidly
At any stage, the equilibrium is not disturbed	Equilibrium may exist only after the completion of the process.
It takes infinite time for completion.	It takes a finite time for completion.
Work obtained in this process is maximum	Work obtained in this process is not maximum*
It is an imaginary process.	It is a natural process

Continue...

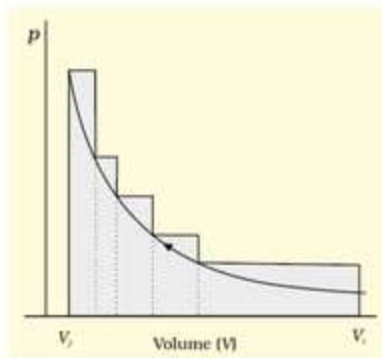
Pressure-Volume Work

- If the compression of gas is carried out in number of finite steps, work done on the gas will be summed over all the steps and will be equal to Σ

$$p\Delta V$$

Fig :-

- pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f*
- Work done on the gas is represented by the shaded area.*



Continue...

Pressure-Volume Work in Reversible process

- If the compression of gas is carried out in infinite steps through reversible process, at each stage of compression, the volume decreases by an infinitesimal amount, dV .
- In this case, the work done on the gas is calculated by the following relation

$$w = - \int_{V_i}^{V_f} p_{ex} dV$$

- Here, p_{ex} at each stage is equal to $(p_{in} + dp)$ in case of compression.
- In an expansion process, $p_{ex} = (p_{in} - dp)$.

$$w_{rev} = - \int_{V_i}^{V_f} p_{ex} dV = - \int_{V_i}^{V_f} (p_{in} \pm dp) dV$$

$$p_{ex} = (p_{in} \pm dp)$$

Since $dp \times dV$ is very small we can write

$$w_{rev} = - \int_{V_i}^{V_f} p_{in} dV = - \int_{V_i}^{V_f} p dV$$

Continue...

Pressure-Volume Work in Reversible process

$$pV = nRT$$

$$w_{\text{rev}} = - \int_{V_i}^{V_f} p \, dV$$

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

$$w_{\text{rev}} = - \int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$w_{\text{rev}} = - 2.303 \, nRT \log \frac{V_f}{V_i}$$

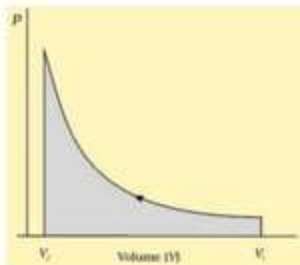


Fig. pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f .

- Work done on the gas is represented by the shaded area.*

Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - Free expansion
 - Problem 6.2, 6.3, 6.4

By Vijay Kumar Sethi

Free expansion:

- Expansion of a gas in vacuum ($p_{\text{ex}} = 0$) is called free expansion.
- No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

$$w = -p_{\text{ex}} \Delta V \quad \text{if } p_{\text{ex}} = 0 \quad w = 0$$

- mathematical statement of the first law of thermodynamics $\Delta U = q + w$

$$\Delta U = q - p_{\text{ex}} \Delta V$$

- If a process is carried out at constant volume ($\Delta V = 0$), then

$$\Delta U = q_v$$

- Change in internal energy is the heat supplied at constant volume.

Isothermal and free expansion of an ideal gas

- For isothermal ($T = \text{constant}$) expansion of an ideal gas into vacuum ; $w = 0$ since $p_{\text{ex}} = 0$.
- Also, Joule determined experimentally that $q = 0$; therefore, ΔU

$\Delta U = q + w = 0$ can be expressed for isothermal irreversible and reversible changes as follows:

$$q = -w = p_{\text{ex}}(V_f - V_i)$$

- For isothermal irreversible change
- For isothermal reversible change $q = -w = nRT \ln \frac{V_f}{V_i} = 2.303 nRT \log \frac{V_f}{V_i}$

$$\Delta U = w_{\text{ad}}$$

- For adiabatic change, $q = 0$

Problem 6.2

Two litres of an ideal gas at a pressure of 10 atm expands isothermally at 25 °C into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

Solution

For isothermal process $q = -w = p_{\text{ex}} (V_f - V_i)$

$w = -p_{\text{ex}} (V_f - V_i) = 0(10 - 2) = 0(8) = 0$ No work is done; no heat is absorbed.

Problem 6.3

Consider the same expansion, but this time against a constant external pressure of 1 atm.

Solution

We have $q = -w = p_{\text{ex}} (8) = 8 \text{ litre-atm}$

Problem 6.4

Consider the expansion given in problem 6.2, for 1 mol of an ideal gas conducted reversibly.

Solutic

$$q = -w = 2.303 nRT \log \frac{V_f}{V_i}$$

$$= 2.303 \times 1 \times 0.0821 \times 298 \log \frac{10}{2}$$

$$= 2.303 \times 1 \times 0.0821 \times 298 \times 0.6990 = 39.38 \text{ L.atm}$$

Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - Enthalpy
 - Relation between ΔU And ΔH

By Vijay Kumar Sethi

Enthalpy, H

- The heat absorbed at constant volume is equal to change in the Internal Energy i.e.,
 $\Delta U = q_v$
- But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure.
- Another thermodynamic function, the enthalpy H [Greek word *enthalpien*, to warm or heat content] as : $H = U + pV$
- Enthalpy is the sum of internal energy and product of pressure-volume.
- Enthalpy is a state function-depends on initial and final states of the system
- Absolute value of H can not be determined.
- Change in enthalpy (ΔH) is determined. $\Delta H = H_2 - H_1$

Continue...

Enthalpy, H

mathematical statement of the first law of thermodynamics $\Delta U = q + w$, $w = -p\Delta V$

At constant pressure, $\Delta U = q_p - p\Delta V$,

where q_p is heat absorbed by the system and $-p\Delta V$ = expansion work done by the system.

Let us consider two state

state 1

state 2

Internal energy

U_1

U_2

Volume

V_1

V_2

Change in internal energy

$$U_2 - U_1 = q_p - p(V_2 - V_1)$$

On rearranging,

$$q_p = (U_2 + pV_2) - (U_1 + pV_1)$$

$$\text{From } H = U + pV$$

$$H_2 = U_2 + pV_2$$

$$H_1 = U_1 + pV_1$$

$$q_p = H_2 - H_1 = \Delta H$$

Continue...

Enthalpy, H

- For finite changes at constant pressure the equation $H = U + pV$ can be written as
- $\Delta H = \Delta U + \Delta pV$ Since p is constant, we can write
- $\Delta H = \Delta U + p\Delta V$
- $\Delta H = q_p$, heat absorbed by the system at constant pressure
- ΔH is negative for exothermic reactions which evolve heat during the reaction and
- ΔH is positive for endothermic reactions which absorb heat from the surroundings.
- At constant volume ($\Delta V = 0$), $\Delta U = q_v$,
- $$\Delta H = \Delta U + p\Delta V \quad \Delta H = q_p = \Delta U = q_v$$
- The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and / or liquids. Solids and liquids do not suffer any significant volume changes upon heating.

Relation between ΔH and ΔU for the system having Gases

- Let us consider a reaction involving gases.
- If V_A = total volume of the gaseous reactants, V_B = total volume of the gaseous products,
- n_A = No. of moles of gaseous reactants, and n_B = No. of moles of gaseous products,
- At constant T and P, $pV_A = n_ART$ and $pV_B = n_BRT$

- Thus, $pV_B - pV_A = n_BRT - n_ART$
 $p(V_B - V_A) = (n_B - n_A)RT$
or $p\Delta V = \Delta n_g RT$

Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

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

$$\Delta H = \Delta U + \Delta n_g RT$$

Problem 6.5

If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and 100°C is 41 kJ mol⁻¹. Calculate the internal energy change, when 1 mol of water is vapourised at 1 bar pressure and 100°C.

Solution

The change $H_2O(l) \rightarrow H_2O(g)$

$$\Delta H = \Delta U + \Delta n_g RT$$

or $\Delta U = \Delta H - \Delta n_g RT$,

$$\Delta H = 41 \text{ kJ mol}^{-1} \quad \Delta n_g = 1 \quad R = 8.3 \text{ JK}^{-1}\text{mol}^{-1} = 8.3 \times 10^{-3} \text{ kJK}^{-1}\text{mol}^{-1} \quad T = 100^\circ\text{C} = 373 \text{ K}$$

$$\Delta U = 41 \text{ kJ mol}^{-1} - 1 \times 8.3 \times 10^{-3} \text{ kJK}^{-1}\text{mol}^{-1} \times 373 \text{ K} = 41 \text{ kJ mol}^{-1} - 3.096 \text{ kJ mol}^{-1}$$

$$\Delta U = 37.904 \text{ kJ mol}^{-1}$$

Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - Extensive and Intensive Properties
 - Measurement Of ΔU And ΔH

By Vijay Kumar Sethi

Extensive and Intensive Properties

- An **extensive property** is a property whose value depends on the quantity or size of matter present in the system.
 - For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.
- Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**.
 - For example temperature, density, pressure, molar heat capacity etc. are intensive properties.

Continue...

Extensive and Intensive Properties

- considering a gas enclosed in a container of volume V and at temperature T .
- Let us make a partition such that volume is halved, each part now has one half of the original volume, $V/2$, but the temperature will still remain the same i.e., T .
- It is clear that volume is an extensive property and temperature is an intensive property.



Fig. A gas at volume V and temperature T

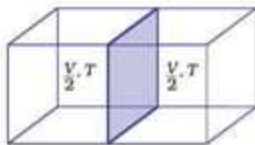


Fig. Partition, each part having half the volume of the gas

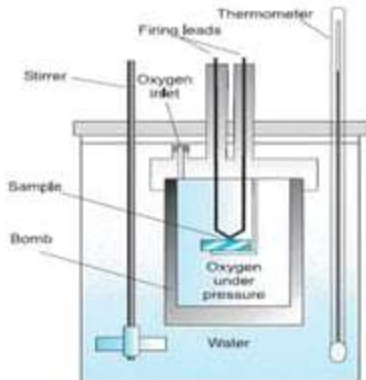
MEASUREMENT OF ΔU AND ΔH :

CALORIMETRY:-

- Experimental technique used to measure energy changes associated with chemical or physical processes is called calorimetry
- A **calorimeter** is a device used to measure the amount of heat changed in a chemical or physical process by measuring temperature changes.
- Measurements are made under two different conditions:
 - i) at constant volume, q_v
 - ii) at constant pressure, q_p

ΔU Measurements

- For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter.
- Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter.
- The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings.
- A combustible substance is burnt in pure dioxygen supplied in the steel bomb



Continue...

ΔU Measurements

- Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored.
- Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume.
- Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter
- Temperature change of the calorimeter produced by the completed reaction is then converted to q_V

ΔH Measurements

- Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a simple calorimeter. $\Delta H = q_p$ (at constant p)
- Heat absorbed or evolved, q_p at constant pressure is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.
- In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, q_p will be negative and $\Delta_r H$ will also be negative.
- Similarly in an endothermic reaction, heat is absorbed, q_p is positive and $\Delta_r H$ will be positive.

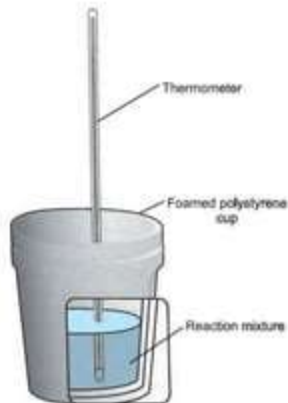


Fig. Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).

Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - *Standard Enthalpy of Reactions*
 - *Enthalpy Changes during Phase Transformations*
 - *Standard Enthalpy of Formation*

By Vijay Kumar Sethi

Enthalpy Change, ΔH Of A Reaction – Reaction Enthalpy

- The enthalpy change accompanying a reaction is called the reaction enthalpy ($\Delta_r H$) or *Enthalpy of a Reaction*.

Standard Enthalpy of Reactions, $\Delta_r H^\ominus$

- The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.
- The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K.
- Standard conditions are denoted by adding the superscript \ominus to the symbol ΔH , e.g., ΔH^\ominus

Enthalpy Changes during Phase Transformations

Standard enthalpy of fusion

- The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{\text{fus}}H^\ominus$.
- Melting of a solid $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$; $\Delta_{\text{fus}}H^\ominus = 6.00 \text{ kJ mol}^{-1}$ is positive

Standard enthalpy of vaporization

- Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its standard enthalpy of vaporization or molar enthalpy $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$; $\Delta_{\text{vap}}H^\ominus = +40.79 \text{ kJ mol}^{-1}$

Continue...

Enthalpy Changes during Phase Transformations

Standard enthalpy of sublimation

- Sublimation is direct conversion of a solid into its vapour.
- $\Delta_{sub}H^\ominus$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar).
- Solid CO_2 or 'dry ice' sublimes at 195K with $\Delta_{sub}H^\ominus=25.2 \text{ kJ mol}^{-1}$;
- Naphthalene sublimes slowly and for this $\Delta_{sub}H^\ominus = 73.0 \text{ kJ mol}^{-1}$
- The magnitude of the enthalpy change depends on the strength of the intermolecular interactions in the substance undergoing the phase transformations.

Problem 6.7

A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K ? Calculate the internal energy of vaporisation at 298K. $\Delta_{\text{vap}} H^\ominus$ for water at 298K = 44.01 kJ mol⁻¹

Solution:- process of evaporation $H_2O(l) \rightarrow H_2O(g)$ 18 g of water = 1 mole of water

Heat supplied to evaporate 18g water at 298 K = $n \times \Delta_{\text{vap}} H^\ominus = (1 \text{ mol}) \times (44.01 \text{ kJ mol}^{-1}) = 44.01 \text{ kJ}$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\text{or } \Delta U = \Delta H - \Delta n_g RT,$$

$$\Delta H = 44.01 \text{ kJ mol}^{-1} \quad \Delta n_g = 1 \quad R = 8.314 \text{ JK}^{-1}\text{mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1}$$

$$T = 298 \text{ K}$$

$$\Delta U = 44.01 \text{ kJ mol}^{-1} - 1 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1} \times 298 \text{ K} = 44.01 \text{ kJ mol}^{-1} - 2.48 \text{ kJ mol}^{-1}$$

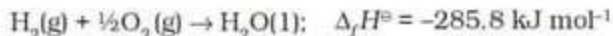
$$\Delta U = 41.53 \text{ kJ mol}^{-1}$$

Standard Enthalpy of Formation

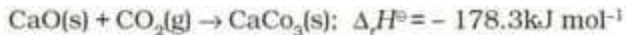
- The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^\ominus$
- The **reference state** of an element is its most stable state of aggregation at 25°C and 1 bar pressure.
- For example, the reference state of dihydrogen is H_2 gas and those of dioxygen, carbon and sulphur are O_2 gas, C_{graphite} and S_{rhombic} respectively.

Continue...

Standard Enthalpy of Formation



- standard molar enthalpy of formation, $\Delta_f H^\ominus$, is just a special case of $\Delta_r H^\ominus$, where one mole of a compound is formed from its constituent elements.

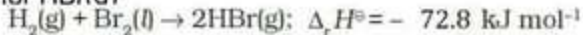


- It is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements.

Continue...

Standard Enthalpy of Formation

- for the reaction given below, enthalpy change is not standard enthalpy of formation, $\Delta_f H^\ominus$ for HBr(g)



- Here two moles, instead of one mole of the product is formed from the elements, i.e.,

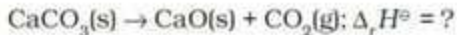
$$\Delta_r H^\ominus = 2\Delta_f H^\ominus$$

- expressing $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{HBr}(\text{g}); \Delta_f H^\ominus = -36.4 \text{ kJ mol}^{-1}$

Continue...

Standard Enthalpy of Formation

- By convention, standard enthalpy for formation, $\Delta_f H^\ominus$, of an **element** in reference state, i.e., its most stable state of aggregation is taken as **zero**.
- How much heat is required to decompose calcium carbonate?



$$\Delta_r H^\ominus = \sum a_i \Delta_f H^\ominus(\text{products}) - \sum b_j \Delta_f H^\ominus(\text{reactants})$$

$$\Delta_r H^\ominus = \Delta_f H^\ominus [\text{CaO}(\text{s})] + \Delta_f H^\ominus [\text{CO}_2(\text{g})] - \Delta_f H^\ominus [\text{CaCO}_3(\text{s})]$$

$$= 1(-635.1 \text{ kJ mol}^{-1}) + 1(-393.5 \text{ kJ mol}^{-1}) - 1(-1206.9 \text{ kJ mol}^{-1})$$

$$= 178.3 \text{ kJ mol}^{-1}$$

decomposition of $\text{CaCO}_3(\text{s})$ is an endothermic process

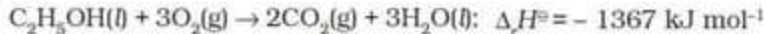
Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - *Thermochemical Equations*
 - *Hess's Law of Constant Heat Summation*

By Vijay Kumar Sethi

Thermochemical Equations

- A balanced chemical equation together with the value of its $\Delta_r H$ is called a thermochemical equation.
- We specify the physical state (along with allotropic state) of the substance in an equation.



- The above equation describes the combustion of liquid ethanol at constant temperature and pressure.
- The negative sign of enthalpy change indicates that this is an exothermic reaction.

Continue...

Thermochemical Equations

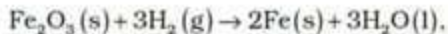
remember the following conventions regarding thermochemical equations.

- 1) The coefficients in a balanced thermochemical equation refer to the number of moles (never molecules) of reactants and products involved in the reaction.
- 2) The numerical value of $\Delta_r H^\ominus$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H^\ominus$ will have units as kJ

- The unit for $\Delta_r H^\ominus$ is kJ mol^{-1} , which means *per mole of reaction*.
- Once we balance the chemical equation in a particular way, this defines the *mole of reaction*.

Continue...

Thermochemical Equations



$$\Delta_f H^\circ (\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ mol}^{-1}; \quad \Delta_f H^\circ (\text{Fe}_2\text{O}_3, \text{s}) = -824.2 \text{ kJ mol}^{-1};$$

$$\Delta_f H^\circ (\text{Fe}, \text{s}) = 0 \text{ and } \Delta_f H^\circ (\text{H}_2, \text{g}) = 0 \text{ as per convention}$$

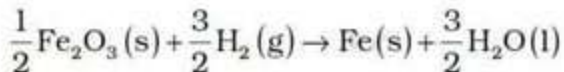
$$\Delta_r H^\circ = \sum a_i \Delta_f H^\circ (\text{products}) - \sum b_i \Delta_f H^\circ (\text{reactants})$$

$$\Delta_r H_1^\circ = 3 \times \Delta_f H^\circ (\text{H}_2\text{O}, \text{l}) + 2 \times \Delta_f H^\circ (\text{Fe}, \text{s}) - [1 \times \Delta_f H^\circ (\text{Fe}_2\text{O}_3, \text{s}) + 3 \times \Delta_f H^\circ (\text{H}_2, \text{g})]$$

$$\begin{aligned} \text{Then, } \Delta_r H_1^\circ &= 3(-285.83 \text{ kJ mol}^{-1}) + 0 - [1(-824.2 \text{ kJ mol}^{-1}) + 0] \\ &= (-857.5 + 824.2) \text{ kJ mol}^{-1} = -33.3 \text{ kJ mol}^{-1} \end{aligned}$$

Continue...

Thermochemical Equations



then this amount of reaction would be one mole of reaction and $\Delta_r H^\ominus$ would be

$$\Delta_r H_2^\ominus = \frac{3}{2}(-285.83 \text{ kJ mol}^{-1}) - \frac{1}{2}(-824.2 \text{ kJ mol}^{-1})$$

$$= (-428.7 + 412.1) \text{ kJ mol}^{-1} = -16.6 \text{ kJ mol}^{-1} = \frac{1}{2} \Delta_r H_1^\ominus$$

It shows that enthalpy is an extensive quantity.

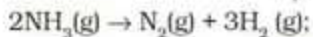
Continue...

Thermochemical Equations

- 3) When a chemical equation is reversed, the value of $\Delta_r H^\ominus$ is reversed in sign. For example



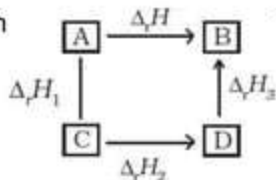
$$\Delta_r H^\ominus = -91.8 \text{ kJ mol}^{-1}$$



$$\Delta_r H^\ominus = +91.8 \text{ kJ mol}^{-1}$$

Hess's Law of Constant Heat Summation

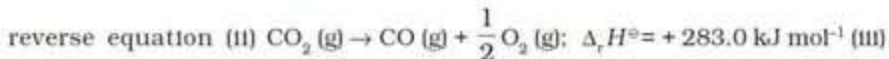
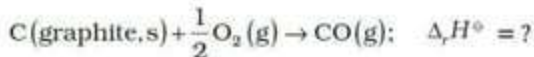
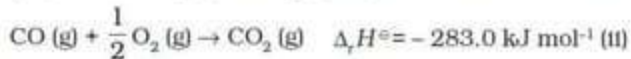
- Enthalpy is a state function
- Enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps.
- Statement:**
 - If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at any temperature.



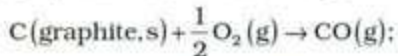
$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$$

Continue...

Hess's Law of Constant Heat Summation



Adding equation (i) and (iii), we get the desired equation,



$$\text{for which } \Delta_r H^\ominus = (- 393.5 + 283.0) = - 110.5 \text{ kJ mol}^{-1}$$

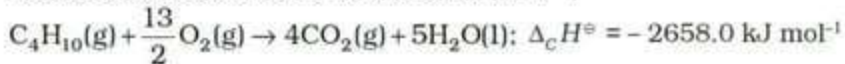
Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - *Standard Enthalpy of Combustion*
 - *Enthalpy of Atomization*
 - *Bond Enthalpy*

By Vijay Kumar Sethi

Standard Enthalpy of Combustion (symbol : $\Delta_c H^\ominus$)

- Combustion reactions are exothermic in nature.
- Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the reactants and products being in their standard states at the specified temperature.
- Cooking gas in cylinders contains mostly C_4H_{10}



Problem 6.9

The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^\ominus$ of benzene.

Standard enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are $-393.5 \text{ kJ mol}^{-1}$ and $-285.83 \text{ kJ mol}^{-1}$ respectively.

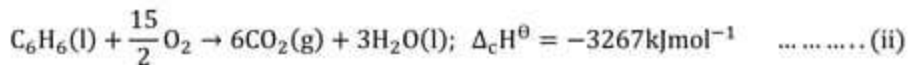
Solution

The formation reaction of benzene is given by :

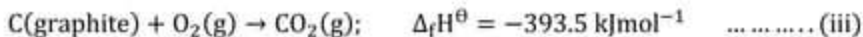


Continue.. Solution of Problem 6.9

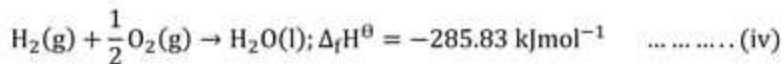
The enthalpy of combustion of 1 mol of benzene is



The enthalpy of formation of 1 mol of $\text{CO}_2(\text{g})$:



The enthalpy of formation of 1 mol of $\text{H}_2\text{O}(\text{l})$ is :

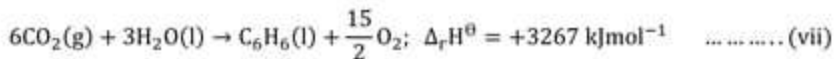
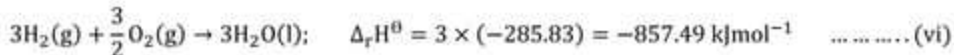
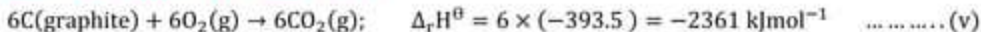


Using equation (ii), (iii) and (iv) we have to bring the following equation (i)

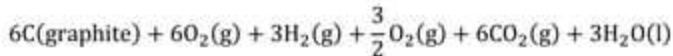


So multiply equation (iii) by 6 and (iv) by 3 and reverse equation (ii)

Continue.. Solution of Problem 6.9



Now add equation (v), (vi) and (vii)

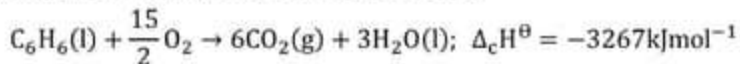


Continue.. Solution of Problem 6.9

Alternate method

$$\Delta_r H^\ominus = \sum a_i \Delta_f H^\ominus(\text{products}) - \sum b_i \Delta_f H^\ominus(\text{reactants})$$

The enthalpy of combustion of 1 mol of benzene is



Given $\Delta_f H^\ominus \text{CO}_2(\text{g}) = -393.5 \text{ kJ mol}^{-1}$ and $\Delta_f H^\ominus \text{H}_2\text{O}(\text{l}) = -285.83 \text{ kJ mol}^{-1}$, $\Delta_f H^\ominus$

$$\text{O}_2(\text{g}) = 0$$

$$\Delta_r H^\ominus = 6 \times \Delta_f H^\ominus(\text{CO}_2) + 3 \times \Delta_f H^\ominus(\text{H}_2\text{O}) - [\Delta_f H^\ominus(\text{C}_6\text{H}_6) + \frac{15}{2} \times \Delta_f H^\ominus(\text{O}_2)]$$

$$-3267 = 6 \times (-393.5) + 3 \times (-285.83) - [\Delta_f H^\ominus(\text{C}_6\text{H}_6) + 0]$$

$$-3267 = -2361 + (-857.49) - [\Delta_f H^\ominus(\text{C}_6\text{H}_6) + 0]$$

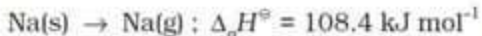
$$\Delta_f H^\ominus(\text{C}_6\text{H}_6) = -3218.49 + 3267 = 48.51 \text{ kJ mol}^{-1}$$

Enthalpy of Atomization (symbol: $\Delta_a H^\ominus$)

- It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.



- In case of diatomic molecules, like dihydrogen, the enthalpy of atomization is also the bond dissociation enthalpy.
- Other examples



In this case, the enthalpy of atomization is same as the enthalpy of sublimation

Bond Enthalpy (symbol: $\Delta_{\text{bond}}H^\ominus$)

(i) Bond dissociation enthalpy

(ii) Mean bond enthalpy

(i) Bond dissociation enthalpy

- For **diatomic molecules** the bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

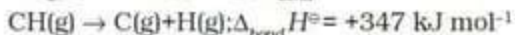
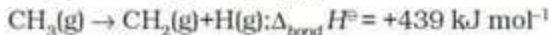
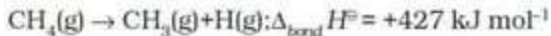


it is the same as the
enthalpy of atomization

(ii) Mean bond enthalpy

- Used for Polyatomic Molecules
- In methane, all the four C – H bonds are identical in bond length and energy.

However, the energies required to break the individual C – H bonds in each



Therefore, $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g}); \Delta_a H^\ominus = 1665 \text{ kJ mol}^{-1}$

$$\Delta_{\text{C-H}} H^\ominus = \frac{1}{4} (\Delta_a H^\ominus) = \frac{1}{4} (1665 \text{ kJ mol}^{-1}) = 416 \text{ kJ mol}^{-1}$$

The standard enthalpy of reaction, $\Delta_r H^\ominus$ is related to bond enthalpies of the reactants and products in gas phase reactions

$$\Delta_r H^\ominus = \sum \text{bond enthalpies}_{\text{reactants}} - \sum \text{bond enthalpies}_{\text{products}}$$

Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - *Lattice Enthalpy*
 - *Born-Haber Cycle*
 - *Enthalpy of Solution*
 - *Enthalpy of Dilution*

By Vijay Kumar Sethi

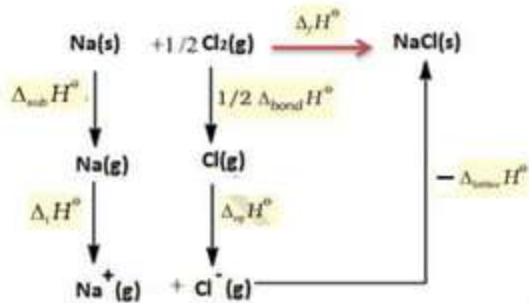
Lattice Enthalpy

- The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.



- Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a **Born-Haber Cycle**

Born Haber Cycle for Sodium Chloride



The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero.

$$\Delta_{\text{sub}}H^{\ominus} = 108.4 \text{ kJ mol}^{-1}$$

$$\Delta_iH^{\ominus} = 496 \text{ kJ mol}^{-1}$$

$$\frac{1}{2} \Delta_{\text{bond}}H^{\ominus} = 121 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{eg}}H^{\ominus} = -348.6 \text{ kJ mol}^{-1}$$

$$\Delta_fH^{\ominus} = -411.2 \text{ kJ mol}^{-1}$$

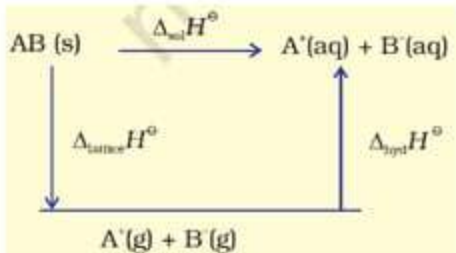
$$\Delta_fH^{\ominus} = \Delta_{\text{sub}}H^{\ominus} + \Delta_iH^{\ominus} + \frac{1}{2} \Delta_{\text{bond}}H^{\ominus} + \Delta_{\text{eg}}H^{\ominus} + (-\Delta_{\text{lattice}}H^{\ominus})$$

$$\Delta_{\text{lattice}}H^{\ominus} = 108.4 + 496 + 121 + (-348.6) + 411.2 = +788 \text{ kJ}$$

$$\text{for } \text{NaCl(s)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \quad \Delta_{\text{lattice}}H^{\ominus} = +788 \text{ kJ}$$

Enthalpy of Solution (symbol : $\Delta_{\text{sol}} H^\ominus$)

- Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent.
- The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.



$$\Delta_{\text{sol}} H^\ominus = \Delta_{\text{lattice}} H^\ominus + \Delta_{\text{hyd}} H^\ominus$$

Continue...

Enthalpy of Solution (symbol : $\Delta_{\text{sol}}H^{\ominus}$)

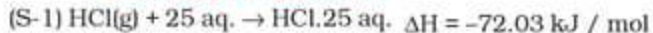
- For most of the ionic compounds, $\Delta_{\text{sol}}H^{\ominus}$ is positive and the dissolution process is endothermic.
- Therefore the solubility of most salts in water increases with rise of temperature.
- If the lattice enthalpy is very high, the dissolution of the compound may not take place at all.

Enthalpy of Dilution

- It is the heat change when additional solvent is added to the solution.
- The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.
- Enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water ($1 \text{ HCl(g)} + 10 \text{ aq.} \rightarrow \text{HCl.10 aq.}$ $\Delta H = -69.01 \text{ kJ / mol}$
(S-1) $\text{HCl(g)} + 25 \text{ aq.} \rightarrow \text{HCl.25 aq.}$ $\Delta H = -72.03 \text{ kJ / mol}$
(S-2) $\text{HCl(g)} + 40 \text{ aq.} \rightarrow \text{HCl.40 aq.}$ $\Delta H = -72.79 \text{ kJ / mol}$
(S-3) $\text{HCl(g)} + \infty \text{ aq.} \rightarrow \text{HCl.} \infty \text{ aq.}$ $\Delta H = -74.85 \text{ kJ / mol}$
- The values of enthalpy of solution depend on amount of solvent.
- Enthalpy of solution approaches a limiting value, i.e, the value in infinitely dilute solution(S-3)

Continue...

Enthalpy of Dilution



Subtract equation S-1 from the equation S-2 we obtain—



$$\Delta H = [-72.79 - (-72.03)] \text{ kJ / mol} = -0.76 \text{ kJ / mol}$$

- This value (-0.76 kJ/mol) of ΔH is enthalpy of dilution.

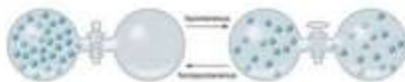
Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - Spontaneous Process
 - *Criterion for Spontaneity-Driving force for spontaneous process*
 - Entropy

By Vijay Kumar Sethi

Spontaneous Process

- A spontaneous process is one that occurs on its own or once started proceeds, without the external input of energy.
- It cannot be reversed on its own. It is unidirectional
- All natural processes are spontaneous.
- For example,
 - a gas expanding to fill the available volume,
 - burning carbon in dioxygen giving carbon dioxide
 - Rolling of ball downhill
 - Rusting of iron
 - Freezing of water at temperatures below 0°C
 - Melting of ice



RUSTING - SPONTANEOUS EXOTHERMIC PROCESS



ICE MELTING - SPONTANEOUS ENDOTHERMIC PROCESS

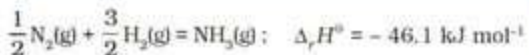


REMOVAL OF SUGAR from a cup of coffee
This is a **NON SPONTANEOUS** process

Criterion for Spontaneity-Driving force for spontaneous

Decrease in Enthalpy

- Spontaneous physical process
 - flow of water down hill
 - fall of a stone on to the ground
- there is a net decrease in potential energy in the direction of



- Exothermic chemical reactions are spontaneous because decrease in energy has taken place
- Driving force for a spontaneous process is 'decrease in energy (enthalpy)' i.e. $-\Delta H$

Continue...

Criterion for Spontaneity-Driving force for spontaneous process

- *Decrease in Enthalpy*

Now examine the following reactions:

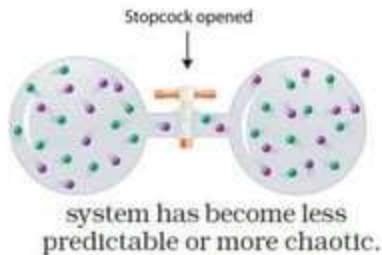
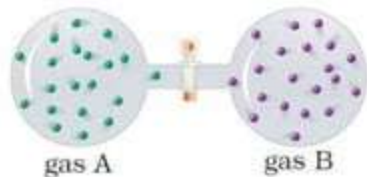
- The reaction between solid barium hydroxide octahydrate and solid ammonium thiocyanate is endothermic and spontaneous.
 - While most acid-base reactions are exothermic, the reaction of baking soda with vinegar is endothermic.
 - Dissolution of Common salt into water is endothermic and spontaneous
- These reactions though endothermic (ΔH is positive), are spontaneous.
 - Therefore, it is concluded that decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

Continue...

Criterion for Spontaneity-Driving force for spontaneous process

Another criteria

- examine such a case in which $\Delta H = 0$ i.e., there is no change in enthalpy, but still the process is spontaneous.
- Consider diffusion of two gases into each other in a closed container which is isolated from the surroundings



Continue...

Criterion for Spontaneity-Driving force for spontaneous process

Another criteria

- We may now formulate another postulate:
- in an isolated system, there is always a tendency for the systems' energy to become more **disordered or chaotic** and this could be a criterion for spontaneous change !
- To express this disorder of system, another thermodynamic term is used which is called **Entropy**

Entropy (S)

- Entropy is a measure of the degree of randomness or disorder in the system.
- The greater the disorder in an isolated system, the higher is the entropy.
- Qualitatively, Order of entropy :-Solid(lowest entropy) < Liquid < gas (highest entropy)
- Entropy is a state function and ΔS is independent of path.
- Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system.
- A system at higher temperature has greater randomness in it than one at lower temperature.
- Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature.
- This suggests that the entropy change is inversely proportional to the temperature.

Continue...

Entropy (S)

- ΔS is related with q and T for a reversible reaction as $\Delta S = \frac{q_{rev}}{T}$
- The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by $\Delta S_{total} = \Delta S_{system} + \Delta S_{sur} > 0$
- When a system is in **equilibrium**, the entropy is **maximum**, and the **change** in entropy, **$\Delta S = 0$** .
- Entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero.
- Since entropy is a state property, $\Delta S_{sys} = \frac{q_{sys,rev}}{T}$ calculate the change in entropy of a reversible process by

Continue...

Entropy (S)

- Both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e., $\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process.
- Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.
- $\Delta S_{total} > 0$ Process is spontaneous
- $\Delta S_{total} < 0$ Process is Non-spontaneous
- $\Delta S_{total} = 0$ System is in equilibrium
- Conclusion:-neither decrease in enthalpy nor increase in entropy of the system alone can determine the direction of spontaneous change for closed and open systems

Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - *Gibbs Energy*
 - Gibbs Energy and Spontaneity
 - Effect of Temperature on Spontaneity of Reactions

By Vijay Kumar Sethi

Gibbs Energy or Gibbs Function, G

- $G = H - TS$ Gibbs function, G is an extensive property and a state function.
- Its absolute value also can not be determined.

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T \quad \text{(be written as)}$$

$$\text{At constant temperature, } \Delta T = 0 \quad \therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{Gibbs equation}$$

ΔG has units of energy i.e J

- ΔH is the enthalpy change of a reaction, $T\Delta S$ is the energy which is not available to do useful work.
- So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'.
- For this reason, it is also known as the free energy of the reaction.

Gibbs Energy and Spontaneity

We know, $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

- If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system.
- Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

• Therefore, entropy $\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$ $\Delta S_{total} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T}\right)$

Rearranging the above equation: $T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$

$$-T\Delta S_{total} = \Delta H_{sys} - T\Delta S_{sys} = \Delta H - T\Delta S$$

We know, $\Delta G = \Delta H - T\Delta S$ $-T\Delta S_{total} = \Delta G$

Continue...

Gibbs Energy and Spontaneity

$$-T\Delta S_{\text{total}} = \Delta G$$

- $\Delta S_{\text{total}} > 0$ Process is spontaneous $\Delta G < 0$
(Negative)
- $\Delta S_{\text{total}} < 0$ Process is Non-spontaneous $\Delta G > 0$
(Positive)
- $\Delta S_{\text{total}} = 0$ System is in equilibrium $\Delta G = 0$
(Equilibrium)

Effect of Temperature on Spontaneity of Reactions

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description
-	+	- (at all T)	Reaction spontaneous at all temperatures
-	-	- (at low T)	Reaction spontaneous at low temperature
-	-	+ (at high T)	Reaction non-spontaneous at high temperature
+	+	+ (at low T)	Reaction non-spontaneous at low temperature
+	+	- (at high T)	Reaction spontaneous at high temperature
+	-	+ (at all T)	Reaction non-spontaneous at all temperatures

Class XI Chemistry
Unit 6
THERMODYNAMICS

- Topic:-
 - Second Law of Thermodynamics
 - Third Law of Thermodynamics
 - Gibbs Energy Change And Equilibrium

By Vijay Kumar Sethi

Entropy and Second Law of Thermodynamics

- **Entropy** is the loss of energy available to do work.
- **Another** form of the **second law of thermodynamics** states that the total **entropy** of a system either increases or remains constant; it never decreases.
- **Entropy** is zero in a reversible process; it increases in an irreversible process.
- Entropy of any isolated system always increases.
- In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

Absolute Entropy and Third Law of Thermodynamics

- The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics.
- The importance of the third law is that absolute values of entropy of pure substance can be determined.

GIBBS ENERGY CHANGE AND EQUILIBRIUM

- Reversible chemical reaction is the reaction which can proceed in either direction simultaneously that is reactants convert into products and products convert in to reactants at the same rate, so that a dynamic equilibrium is set up.
- This means that the reactions in both the directions should proceed with a decrease in free energy, which seems impossible.
- It is possible only if at equilibrium the free energy of the system is minimum.
- So, the criterion for equilibrium



Continue...

GIBBS ENERGY CHANGE AND EQUILIBRIUM

- Gibbs energy change for a reaction in which all reactants and products are in standard state, is known as Standard Gibbs energy change $\Delta_r G^\ominus$
- It is related to the equilibrium constant of the reaction as follows:

$$\Delta_r G = \Delta_r G^\ominus + RT \ln K \quad \text{at equilibrium } \Delta_r G = 0 \quad \text{so, } \Delta_r G^\ominus = -RT \ln K$$

$$\text{or } \Delta_r G^\ominus = -2.303 RT \log K \quad \text{where } K = \text{equilibrium constant}$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus = -2.303 RT \log K$$

- For strongly endothermic reactions, the $\Delta_r H^\ominus$ large and positive, value of $K \ll 1$ and the reaction is unlikely to form much product.
- In case of exothermic reactions, $\Delta_r H^\ominus$ large and negative, and $\Delta_r G^\ominus$ large and negative, $K \gg 1$ hence can go to near completion.

Problem 6.12

Calculate $\Delta_r G^\ominus$ for conversion of oxygen to ozone, $3/2 \text{ O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$ at 298 K. if K_p for this conversion is 2.47×10^{-29} .

Solution

We know $\Delta_r G^\ominus = -2.303 RT \log K_p$ and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\begin{aligned}\text{Therefore, } \Delta_r G^\ominus &= -2.303 (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) (\log 2.47 \times 10^{-29}) \\ &= 163000 \text{ J mol}^{-1} \quad = 163 \text{ k J mol}^{-1}\end{aligned}$$

Problem 6.13

Find out the value of equilibrium constant for the following reaction at 298 K.



Standard Gibbs energy change, $\Delta_r G^\ominus$ at the given temperature is -13.6 kJ mol⁻¹.

Solution

$$\Delta_r G^\ominus = -2.303 RT \log K$$

$$\log K = -\frac{\Delta_r G^\ominus}{2.303 RT} = -\frac{-13.6 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 2.38$$

$$K = \text{antilog } 2.38 = 2.4 \times 10^2$$

How to Solve log and antilog

By Vijay
Kumar Sethi

LOGARITHM TABLES

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
00	0000	0043	0086	0128	0170	0212	0253	0294	0335	0376	4	5	12	17	22	27	32	37	42	47
01	0414	0457	0499	0541	0582	0623	0664	0705	0746	0786	6	7	11	15	19	23	27	31	35	39
02	0792	0833	0874	0914	0954	0994	1034	1074	1113	1152	8	9	13	17	21	25	29	33	37	41
03	1191	1229	1267	1304	1341	1378	1414	1450	1486	1521	10	11	15	19	23	27	31	35	39	43
04	1558	1594	1629	1664	1699	1734	1769	1803	1837	1871	12	13	17	21	25	29	33	37	41	45
05	1905	1938	1971	2003	2035	2067	2099	2130	2161	2192	14	15	19	23	27	31	35	39	43	47
06	2223	2253	2283	2312	2341	2370	2399	2427	2455	2483	16	17	21	25	29	33	37	41	45	49
07	2511	2539	2566	2593	2620	2646	2672	2698	2724	2750	18	19	23	27	31	35	39	43	47	51
08	2775	2800	2825	2850	2875	2900	2925	2950	2975	3000	20	21	25	29	33	37	41	45	49	53
09	3025	3050	3075	3100	3125	3150	3175	3200	3225	3250	22	23	27	31	35	39	43	47	51	55
10	3275	3300	3325	3350	3375	3400	3425	3450	3475	3500	24	25	29	33	37	41	45	49	53	57

ANTI LOGARITHM TABLES

	0	1	2	3	4	5	6	7	8	9	Mean difference								
											1	2	3	4	5	6	7	8	9
00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
01	1023	1026	1029	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2

LOGARITHM TABLES

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0129	0172	0215	0258	0301	0344	0387	4	0	12	15	21	26	31	36	41
11	0424	0467	0510	0553	0596	0639	0682	0725	0768	0811	5	0	13	16	22	27	32	37	42
12	0850	0893	0936	0979	1022	1065	1108	1151	1194	1237	6	0	14	17	23	28	33	38	43
13	1259	1302	1345	1388	1431	1474	1517	1560	1603	1646	7	0	15	18	24	29	34	39	44
14	1689	1732	1775	1818	1861	1904	1947	1990	2033	2076	8	0	16	19	25	30	35	40	45
15	2119	2162	2205	2248	2291	2334	2377	2420	2463	2506	9	0	17	20	26	31	36	41	46
16	2549	2592	2635	2678	2721	2764	2807	2850	2893	2936	10	0	18	21	27	32	37	42	47
17	2979	3022	3065	3108	3151	3194	3237	3280	3323	3366	11	0	19	22	28	33	38	43	48
18	3409	3452	3495	3538	3581	3624	3667	3710	3753	3796	12	0	20	23	29	34	39	44	49
19	3839	3882	3925	3968	4011	4054	4097	4140	4183	4226	13	0	21	24	30	35	40	45	50
20	4269	4312	4355	4398	4441	4484	4527	4570	4613	4656	14	0	22	25	31	36	41	46	51
21	4698	4741	4784	4827	4870	4913	4956	4999	5042	5085	15	0	23	26	32	37	42	47	52
22	5128	5171	5214	5257	5300	5343	5386	5429	5472	5515	16	0	24	27	33	38	43	48	53
23	5558	5601	5644	5687	5730	5773	5816	5859	5902	5945	17	0	25	28	34	39	44	49	54
24	5988	6031	6074	6117	6160	6203	6246	6289	6332	6375	18	0	26	29	35	40	45	50	55
25	6418	6461	6504	6547	6590	6633	6676	6719	6762	6805	19	0	27	30	36	41	46	51	56
26	6848	6891	6934	6977	7020	7063	7106	7149	7192	7235	20	0	28	31	37	42	47	52	57
27	7278	7321	7364	7407	7450	7493	7536	7579	7622	7665	21	0	29	32	38	43	48	53	58
28	7708	7751	7794	7837	7880	7923	7966	8009	8052	8095	22	0	30	33	39	44	49	54	59
29	8138	8181	8224	8267	8310	8353	8396	8439	8482	8525	23	0	31	34	40	45	50	55	60
30	8568	8611	8654	8697	8740	8783	8826	8869	8912	8955	24	0	32	35	41	46	51	56	61
31	9036	9079	9122	9165	9208	9251	9294	9337	9380	9423	25	0	33	36	42	47	52	57	62
32	9466	9509	9552	9595	9638	9681	9724	9767	9810	9853	26	0	34	37	43	48	53	58	63
33	9896	9939	9982	10000							27	0	35	38	44	49	54	59	64
34											28	0	36	39	45	50	55	60	65
35											29	0	37	40	46	51	56	61	66
36											30	0	38	41	47	52	57	62	67
37											31	0	39	42	48	53	58	63	68
38											32	0	40	43	49	54	59	64	69
39											33	0	41	44	50	55	60	65	70
40											34	0	42	45	51	56	61	66	71
41											35	0	43	46	52	57	62	67	72
42											36	0	44	47	53	58	63	68	73
43											37	0	45	48	54	59	64	69	74
44											38	0	46	49	55	60	65	70	75
45											39	0	47	50	56	61	66	71	76
46											40	0	48	51	57	62	67	72	77
47											41	0	49	52	58	63	68	73	78
48											42	0	50	53	59	64	69	74	79
49											43	0	51	54	60	65	70	75	80
50											44	0	52	55	61	66	71	76	81
51											45	0	53	56	62	67	72	77	82
52											46	0	54	57	63	68	73	78	83
53											47	0	55	58	64	69	74	79	84
54											48	0	56	59	65	70	75	80	85
55											49	0	57	60	66	71	76	81	86
56											50	0	58	61	67	72	77	82	87
57											51	0	59	62	68	73	78	83	88
58											52	0	60	63	69	74	79	84	89
59											53	0	61	64	70	75	80	85	90
60											54	0	62	65	71	76	81	86	91
61											55	0	63	66	72	77	82	87	92
62											56	0	64	67	73	78	83	88	93
63											57	0	65	68	74	79	84	89	94
64											58	0	66	69	75	80	85	90	95
65											59	0	67	70	76	81	86	91	96
66											60	0	68	71	77	82	87	92	97
67											61	0	69	72	78	83	88	93	98
68											62	0	70	73	79	84	89	94	99
69											63	0	71	74	80	85	90	95	100
70											64	0	72	75	81	86	91	96	100
71											65	0	73	76	82	87	92	97	100
72											66	0	74	77	83	88	93	98	100
73											67	0	75	78	84	89	94	99	100
74											68	0	76	79	85	90	95	100	100
75											69	0	77	80	86	91	96	100	100
76											70	0	78	81	87	92	97	100	100
77											71	0	79	82	88	93	98	100	100
78											72	0	80	83	89	94	99	100	100
79											73	0	81	84	90	95	100	100	100
80											74	0	82	85	91	96	100	100	100
81											75	0	83	86	92	97	100	100	100
82											76	0	84	87	93	98	100	100	100
83											77	0	85	88	94	99	100	100	100
84											78	0	86	89	95	100	100	100	100
85											79	0	87	90	96	100	100	100	100
86											80	0	88	91	97	100	100	100	100
87											81	0	89	92	98	100	100	100	100
88											82	0	90	93	99	100	100	100	100
89											83	0	91	94	100	100	100	100	100
90											84	0	92	95	100	100	100	100	100
91											85	0	93	96	100	100	100	100	100
92											86	0	94	97	100	100	100	100	100
93											87	0	95	98	100	100	100	100	100
94											88	0	96	99	100	100	100	100	100
95											89	0	97	100	100	100	100	100	100
96											90	0	98	100	100	100	100	100	100
97											91	0	99	100	100	100	100	100	100
98											92	0	100	100	100	100	100	100	100
99											93	0	100	100	100	100	100	100	100
100											94	0	100	100	100	100	100	100	100

$$\log \frac{n}{m} = \log n - \log m$$

$$\log(n \times m) = \log n + \log m$$

$$\log x^n = n \log x$$

$$\log 2467 = 3.3909 + 0.0012 = 3.3921$$

$$\log 382.4 = 2.5821 + 0.0005 = 2.5826$$

$$\log 55.2 = 1.7419$$

$$\log 2.03 = 0.3075$$

$$\log 0.02453 = \log(2.453 \times 10^{-2}) = \log 2.453 + \log 10^{-2}$$

Anti-log table

	0	1	2	3	4	5	6	7	8	9	Mean difference								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	2	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	2	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	2	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	2	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	2	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	2	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	2	2	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	2	2	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	1	2	2	2	2	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	1	2	2	2	2	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	1	2	2	2	2	3
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	1	2	2	2	2	3
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	1	2	2	2	2	3
.36	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.37	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.38	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.39	3890	3899	3908	3917	3926	3935	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.40	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8

$$\text{antilog } 5.2345 = 1.716 \times 10^5$$

$$\text{antilog } 15.5933 = 3.92 \times 10^{15}$$

$$\text{antilog } 15 = \text{antilog } 15.000 = 1.000 \times 10^{15}$$

$$\text{antilog}(-4.42) = ?$$

$$-4.42 = -4.00 - 0.42$$

$$-1 \quad + 1$$

$$-4.42 = -5.00 + 0.58 = \overline{5}.58$$

$$\text{antilog}(-4.42) = \text{antilog}(\overline{5}.58)$$

$$= 3.802 \times 10^{-5}$$