At glance to Chemical Thermodynamics

Laws, state and path functions and their applications; thermodynamic description of various types of processes; Maxwell's relations; spontaneity and equilibria; temperature and pressure dependence of thermodynamic quantities

2.7.1. Chemical Thermodynamics

Key Statement

Basic Key Points: System (2.7.1.1), Surroundings (2.7.1.2), Types of System(2.7.1.4), Properties of system (2.7.1.5), Work and Heat (2.7.1.12), Internal Energy (2.7.1.14), Zeroth law of thermodynamics (2.7.1.16), Enthalpy (2.7.1.21), Adiabatic work (2.7.1.26), Second law of thermodynamics (2.7.1.29), Heat engine and refrigerator (2.7.1.30), Entropy (2.7.1.34), Helmhotz free energy (2.7.1.42), Gibbs free energy (2.7.1.43), Clapeyron equation (2.7.1.51)

Standard Key Point: Various type of thermodynamic process (2.7.1.7), Partial derivative (2.7.1.8), Cyclic rule (2.7.1.9), State function (2.7.1.10), Path function ((2.7.1.11), Some special form of first law (2.7.1.18), Heat capacity (2.7.1.22), Some fundamental relation (2.7.1.45), Chemical potential (2.7.1.49), Clausius – Clapeyron equation (2.7.1.52)

Advance Key Point: Joule – Thomson effect (2.7.1.25), Carnot cycle (2.7.1.31), Carnot theorem (2.7.1.33), Clausius inequality (2.7.1.35), 2.7.1.37 to 2.7.1.41, Criteria for feasibility of a process (2.7.1.44), Maxwell relationship (2.7.1.48)

Key Facts

The term 'Thermo' means heat and 'dynamics' means motion. Therefore, thermodynamics is a branch of science concerned with the flow of heat and deals with the quantitative relationship between heat and other forms of energy in physicochemical transformations.

2.7.1.1. **System:** A thermodynamic system is defined as an object or a quantity of matter i.e., a part of universe which is selected for thermodynamics consideration.

2.7.1.2. **Surrounding:** The remaining part of the universe outside the boundary of the system are called the surroundings.

2.7.1.3. **Types of boundaries for walls:**
   A. **Permeable wall:** A wall that allows the passage of both matter and energy through it.
   B. **Diathermal wall:** A wall that prevents the passage of matter but allows the flow of energy through it.
   C. **Adiabatic wall:** A wall that neither allows the passage of energy or matter through it

2.7.1.4. **Types of systems:**
   A. **Open system:** A system which can exchange matter as well as energy with the surroundings is called an open system.
      Evaporation of water from a beaker represents an open system.
   B. **Closed system:** A system which may exchange energy but not matter with surroundings is called closed system.
      Boiling of water in a closed metallic vessel is an example of closed system.
   C. **Isolated system:** A system which can neither exchange matter or energy with the surroundings is called an isolated system.
      Boiling of water in an insulated system is an example of isolated system.

2.7.1.5. **Properties of system:**
   The physical characteristics which are experimentally measurable and which helps us to define a system are called thermodynamic properties of the system.

A. **Extensive properties:** The properties which depend on the mass of the system are called extensive properties.

e.g., volume, internal energy, enthalpy, entropy, free energy, heat capacity etc.

B. **Intensive properties:** The properties of the system which are independent of mass of the system are called intensive properties.

e.g., temperature, pressure, density, dipole moment, EMF, refractive index, coefficient of viscosity, surface tension, molar volume, chemical potential etc.

2.7.1.6. **Thermodynamic equilibrium:**

A system is said to be in thermodynamic equilibrium if the properties of the system in various phases do not undergo any change with time.

Thermodynamic equilibriums are following types

A. **Thermal equilibrium:** A system is said to be in thermal equilibrium if there is no flow of heat from one portion of the system to another. This is possible only if the temperature remains same throughout in all parts of the system.

B. **Mechanical equilibrium:** A system is said to be in mechanical equilibrium if no mechanical work is done by one part of the system on another part of the system. This is possible only if the pressure remains constant throughout in all parts of the system.

C. **Chemical equilibrium:** A system is said to be in chemical equilibrium if the composition of the various phases in the system does not change with time or chemical potential is same throughout.

D. **Quasiequilibrium process:** A system is said to be in a quasiequilibrium process if the deviation from the thermodynamic equilibrium is infinitesimal.

2.7.1.7. **Various types of thermodynamic processes:**

the operation which brings about the change in the state of the system is called the process.

A. **Isothermal process:** A process that is carried out under conditions of constant temperature is called an isothermal process.

For isothermal process $dT = 0$

B. **Adiabatic process:** A process in which there is no change of heat between the system and surroundings is known as an adiabatic process.

For adiabatic process $dq = 0$

Adiabatic process occurs in isolated system.

C. **Isobaric process:** A process that is carried out under the condition of constant pressure is called isobaric process or isopistic process.

For isobaric process $dP = 0$

D. **Isochoric process:** A process is said to be isochoric if the volume of the system remains constant during the process.

For isochoric process $dV = 0$

E. **Cyclic process:** A process is said to be a cyclic process if a system after completing a series of changes returns to its original state.

F. **Reversible or Quasi-static process:** A reversible process is one which is allowed to happen extremely slowly in infinite step until the whole of the specified changed is achieved and during the change the system does not David from equilibrium bi more than an infinitesimal amount.

Reversible process is ideal and cannot be realised in practice.

Characteristics of reversible process are

    i.   A reversible process occurs very slowly in infinite step until the whole of the specified change is achieved.

    ii.   In reversible process the system does not deviate from equilibrium by more than an infinitesimal amount during the change.

    iii.   Work obtained during expansion is maximum and work done during compression is minimum.

    iv.   Irreversible process can be reversed at any stage by increasing the opposite force by an infinitesimal amount.

G. **Irreversible process:** A process that occurs suddenly and spontaneously such that it does not remain in equilibrium during the transformation is called an irreversible process.

All-natural process like (a) flow of heat from high temperature to low temperature (b) expansion of gas from higher pressure to lower pressure (c) free mixing of gases are irreversible.

In an irreversible process the changes taking place in direct process cannot be reversed.

2.7.1.8. **Partial derivative:** The derivative of a function with respect to one of the independent variables when all other independent variables are kept constant is called partial derivative.

If $x = f(y, z)$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{dx}{dz}\right)_y dz$$

Here $\left(\frac{\partial x}{\partial y}\right)_z$ and $\left(\frac{dx}{dz}\right)_y$ are partial derivatives or partial differentials.

2.7.1.9. **Cyclic rule:** If any three variables (x, y and z) are connected by a functional relationship then the three partial derivatives are connected by following relation $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{dy}{dz}\right)_x \left(\frac{dz}{dx}\right)_y = -1$ and this is known as cyclic rule.

NOTE: P, V, T are function of each other, so $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{dV}{dT}\right)_P \left(\frac{dT}{dP}\right)_V = -1$

2.7.1.10. **State function or characteristic function:**

The function whose magnitude is governed only by the state of the system and whose change of values is independent of path of transformation is called state function.

Internal energy (U), Enthalpy (H), Gibbs free energy (G), entropy pressure temperature volume chemical potential etc. are state function.

Differential of state function is perfect or exact differential.

2.7.1.11. **Path function:**

The function whose magnitude is independent on the path of transformation of the system is called path function.

Function like hit change or work involved in a process depend on the path of transformation of the system are called path functions.

2.7.1.12. **Work and heat:**

❖ **Heat (q):** Energy change it during a process can take place in the form of heat if there is difference in temperature between the system and the surroundings.

A body at higher temperature at transfers heat energy to the body at lower temperature. This takes place through molecular motion thermal equilibrium till established.

➢ Sign Convention: q is positive if heat is absorbed by the system and negative if heat is evolved.

❖ **Work:** Work is said to be done when ever the point of application of a force is displaced in the direction of force.

If F is the magnitude of force and d the displacement of the point of application in the direction in which the force at then the work done is given by $w = F \times d$

There are many kinds of work some of this are: -

I.   Gravitational work (mgh)

II. Electrical work [**E volt** $\times$ **Q qoulomb = EQ joule**]

III. Mechanical work or pressure volume work (PdV)

➢ Sign Convention: According to the latest IUPAC recommendations, positive sign is assigned to the work done on the system and negative sign is assigned to the work done by the system.

2.7.1.13. **Some important point to remember regarding heat and work:**

i.   Both heat and work appear only during the change of state.

ii. Both heat and work are algebraic quantities.

iii. Both heat and work originate only on the boundary of the system.

iv. Both heat and work arise due to an effect on the surroundings.

v.   both heat and work are path function and their differences are not perfect and denoted by $đq$ and $đw$.

2.7.1.14. **Internal Energy (U):** Every system in the universe is a store house of energy by virtue of its position, structure and molecular motion. This energy is called internal or intrinsic energy of the system.

According to the latest IUPAC recommendation internal energy is denoted by U.

It is a state function and therefore its differential is perfect.

2.7.1.15. **Pressure – Volume Work:** If a gas enclosed in a cylinder fitted with frictionless piston, then the work done by the gas, **dw = -P_{ext}dV**, where P is the external pressure and dV be the change in volume due to the expansion of the gas.

> If the gas expands from initial volume V_1 to final volume V_2, the work, $w = \int_{V_1}^{V_2} -P_{ext}dV$

> Work done against vacuum is 0, as $P_{ext} = 0$

2.7.1.16. **Zeroth law of thermodynamics (law of thermal equilibrium):** If two closed systems separately are in thermal equilibrium with a third one, they are in thermal equilibrium with each other.

2.7.1.17. **First law of Thermodynamics (Law of Conservation of Energy):** This law was first of all stated by Mayer and Helmholtz (1840). This law may be stated in any one of the following ways

* Energy can neither be created nor destroyed by any physical or chemical change. However, one form of energy changed into equivalent amount of other form.
* The sum of all forms of energy in isolated system is constant
* Total energy of universe is constant.
* The total mass and energy of an isolated system remains unchanged.

Mathematical form: $\Delta U = q + w$……….(1).

For infinitesimal change the eqn. (1) can be written as dU $= đq + đw$………(2)

Again, if the system does pressure volume work then eqn. (1) & (2) becomes

$\Delta U = q - P\Delta V$ for finite change

$dU = đq – PdV$ for infinitesimal change

2.7.1.18. **Some special forms of the first law:**
a. For isochoric process $\Delta V = 0$, i.e., $\Delta U = q_v$
b. For an isothermal process, $\Delta U = 0$, i.e., $q = -w$
c. For an adiabatic process, dq=0, i.e., $\Delta U = w$
d. For isobaric process, $\Delta U = q - P\Delta V$, i.e., $\Delta U + P\Delta V = q_p = \Delta H$
e. For a cyclic process, dU = 0.

2.7.1.19. **Work done in reversible process (Quasi-static process)**

- For n moles of an ideal gas during isothermal reversible expansion work, $w_{rev} = -nRT \ln {V_2}/{V_1}$.

- For n moles of vander Waals gas during isothermal reversible expansion work, $w_{rev} = -\left[nRT \ln \frac{V_2}{V_1} + n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \right]$.

2.7.1.20. **Work done for irreversible expansion of ideal gas:**

- For n mole of an ideal gas during isothermal irreversible expansion, $w_{irr} = -nRT \left(1 - \frac{P_2}{P_1} \right)$

- For n mole of an ideal gas duringnon-isothermal irreversible expansion, $w_{irr} = -nR \left(T_2 - T_1 \frac{P_2}{P_1} \right)$.

Always keep in mind that $|w_{rev}| > |w_{irrev}|$

2.7.1.21. **Enthalpy (H):**

Change at constant volume permit to calculate ΔU. however most of the reactions are carried out in open latest at constant atmospheric pressure. Under these conditions' changes can occur and work done is equal to PΔV. To avoid the necessity of considering PV work when heat of reactionsis measured at constant pressure we define in Newton and property called heat content or enthalpy.

So basically, enthalpy is defined as total heat content of the system at constant pressure.

Mathematically H = U + PV

Characteristics of enthalpy:

 i.   Absolute value of enthalpy of a system cannot be determined just like the internal energy.
 ii.   Enthalpy is an extensive property.
 iii. Enthalpy is a state function.
 iv.   Change in enthalpy is equal to change of heat at constant pressure.

For n mol of an ideal gas, $\left(\partial U / \partial V \right)_T = 0$, and for n mol Vander Wall's gas, $\left(\partial U / \partial V \right)_T = \frac{n^2 a}{V^2}$.

2.7.1.22. **Heat capacity:** Change in heat due to unit change of temperature is known as heat capacity. This is two kinds, (a) Heat capacity at constant pressure (C_p), (b) Heat capacity at constant volume (C_v)

$C_p - C_v = nR$ for n mol of ideal gas and, $C_P - C_V \cong R + \frac{2aP}{RT^2}$ for n mol of Vander Wall's gas.

2.7.1.23. **Joule's Experiment:** Joule states that **the internal energy of an ideal gas depends only on temperature and independent of volume**.

Mathematically $\left(\frac{\partial U}{\partial V}\right)_T = 0$

2.7.1.24. For n mol of Vander Wall's gas $dU = nC_v dT + \frac{n^2 a}{V^2}$.

2.7.1.25. **Joule – Thomson Effect:** When a gas is allowed to expand through a throttle, i.e., a porous plug made of cotton or silk from high pressure to low pressure under adiabatic condition it is observed that the temperature of the gas increases or decreases. "**The change in temperature accompanying the expansion of a gas through a porous plug into a region of low pressure is known as joule Thomson**".

❖ **Joule Thomson coefficient (μ_{JT}):** It is defined as the temperature is changed in degrees produced by a drop of one atmospheric pressure when the gas expands under condition of constant enthalpy.

Mathematically Joule Thomson coefficient, $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$

❖ **Inversion temperature:** For every gas there is a certain temperature below which cooling and above which heating is observed on Joule Thomson expansion. This temperature is called inversion temperature (T_i). Mathematically, $T_i = \frac{2a}{Rb}$

2.7.1.26. **Adiabatic work:** The process which proceeds under constant heat is known as adiabatic process. For an ideal gas adiabatic work, $W_{ad} = nC_v(T_2 - T_1)$ and for expansion of gas, $w_{ad} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$.

❖ Adiabatic relationship:
  ♣ $PV^\gamma = constant$
  ♣ $TV^{\gamma - 1} = constant$
  ♣ $TP^{\frac{1-\gamma}{\gamma}} = constant$, where, γ is 1.67 for monoatomic gas, 1.6 for diatomic gas, 1.3 for triatomic gas.

2.7.1.27. **Always adiabatic P vs V curve is steeper than isothermal P vs V curve.**

2.7.1.28. Limitations first law of thermodynamics:

i. The first law establishes the relation between the heat absorbed and the work performed by a system. However, it remains silence regarding direction of flow of heat.

ii. according to first law of thermodynamics the energy of an isolated system is conserved during is specified change of state. how it feels to predict whether a specified process or change including a chemical reaction occurs spontaneously.

iii. First law of thermodynamics says that one form of energy can be converted into equivalent amount of energy of another form. However, it does not tell about the ease or extend of convertibility of one form of energy into another.

2.7.1.29. **Second law of thermodynamics:**

Different statements are there among them three are mostusable: -

➢ **Plank – Kelvin Statement:**Heat cannot be converted completely into work in a cyclic process (without changing the state of any other body).

➢ **Calusius Statement:** Heat by itself cannot pass from a lower to higher temperature.

➢ **Thomson Statement:** The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work.

2.7.1.30. **Heat engine & Refrigerator:** The machine used for the conversion of heat into work is called heat engine and refrigerator is a device which takes away heat from the coldest reservoir and with the help of external work the heat is conveyed to the high temperature reservoir.

Efficiency of heat engine, $\eta = \dfrac{\text{Total work done by system}}{\text{Heat absorbed by the system}} = \dfrac{-w_{total}}{Q_1}$

Efficiency of refrigerator, $\varphi = \dfrac{\text{Heat withdrawn from low temperature reservoir}}{\text{Work reqired}} = \dfrac{|Q_1|}{|w|}$

2.7.1.31. Carnot Cycle (Efficiency of Heat Engine):

It is supposing that there are two heat reservoirs, one at a high temperature T_1, known as source and another at lower temperature T_2, known as sink. Now after performing four reversible steps –

a. Isothermal reversible expansion of gas:
$(P_1, V_1, T_1) \rightarrow (P_2, V_2, T_1)$

b. Adiabatic reversible expansion of gas:
$(P_2, V_2, T_1) \rightarrow (P_3, V_3, T_2)$

c. Isothermal reversible compression of gas:
$(P_3, V_3, T_2) \rightarrow (P_4, V_4, T_2)$

d. Adiabatic reversible compression of gas:
$(P_4, V_4, T_2) \rightarrow (P_1, V_1, T_1)$
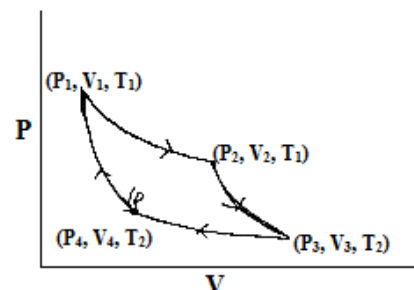
Efficiency of Heat Engine, $\eta = \dfrac{-w_{total}}{Q_1} = \dfrac{T_1 - T_2}{T_1}$

2.7.1.32. Conclusion derived from carnot cycle:

1. Current efficiency is depending only upon the temperature of the two reservoirs with which the engine exchange heat. The efficiency is not dependent upon the nature of the thermodynamics or working substance. Therefore, efficiency will be same whether the substance is ideal for real gas or a liquid or vapour.

2. Since the engine withdraw Q_1 quantity of heat from source at T_1 and religious Q_2 amount of heat to sink at T_2, $\dfrac{|Q_2|}{T_2} = \dfrac{|Q_1|}{T_1}$

3. The efficiency of a carnot engine can be increased either by increasing the temperature of source or by lowering the temperature of sink. The rate of increase of the efficiency can be done by the increasing of source temperature.

2.7.1.33. Carnot theorem:

1. A reversible engine is more efficient than an irreversible engine working between the same temperature limit.

2. All reversible engines are equally efficient working between the same temperature limits.

2.7.1.34. **Entropy:**

Entropy of a system is a function of state who change is measured by the ratio of heat change to the temperature at which the heat change occurs in a reversible process.

Mathematically, $S = \int dS = \int \dfrac{dq_{rev}}{T}$

Unit Jk^{-1} or $cal.deg^{-1}$

Fundamental characteristics of entropy:

i.   Entropy is the property of a substance which measures the disorder or randomness in a system.

ii. Entropy is the capacity factor of unavailable portion of heat energy.

iii. It is a state function and extensive property.

iv. Entropy change cannot be calculated by heat change associated with irreversible change.

v.   entropy change for reversible adiabatic transformation is zero. Show reversible adiabatic changes are isoentropic.

vi. For a closed or open system entropy change of the system is associated with entropy change of the surroundings.

All natural process are spontaneous i.e. irreversible entropy of the universe gradually increases.

2.7.1.35. **Calusius Inequality:** $\int_{A}^{B} \dfrac{dq_{irr}}{T} < \Delta S$

This inequality is known as the Clausius inequality.

For reversible cyclic process $\oint \dfrac{dq}{T} = 0$

For irreversible cyclic process $\oint \dfrac{dq}{T} < 0$

So, for all the process $\oint \dfrac{dq}{T} \leq 0$ 0 for a system in a cyclic process cannot exceed zero.

2.7.1.36. **Second law of thermodynamics in terms of entropy:**

The entropy of the universe is gradually increasing and tends to a maximum value.

2.7.1.37. **Entropy change of an ideal gas:**

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$
$$\Delta S = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_2}{P_1}$$

2.7.1.38. Entropy change for heating or cooling a body:

$$\Delta S = ms \ln \frac{T_2}{T_1}$$

2.7.1.39. Entropy change during transition of state:

$$\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{tr}}{T} = \frac{L_t}{T}$$

2.7.1.40. Entropy change in a chemical reaction:

$$\Delta S = \sum S_P - \sum S_R$$

2.7.1.41. Entropy of mixing of an ideal gas:

$$\Delta_{mix}S = -nR \sum x_i \ln x_i$$

The value of $\Delta_{mix}S/mole$ will be maximum if the components will be taken in equal mole fraction.

2.7.1.42. Helmholtz free energy or work function(A):

Work function is a thermodynamic property of a system whose decrease indicates that irreversible maximum work available during isothermal transformation.

i.e., $-\Delta A = w_{rev}$

A = U – TS

A is a state function, an extensive property.

2.7.1.43. Gibbs free energy or Gibbs potential or Thermodynamic potential (G):

Gibbs free energy is a property that provides a convenient measure of driving force of a transformation. Knowing its change of a system it is possible to predict the spontaneity or feasibility of a process.

The degrees of Gibbs free energy measure the external or net-work is available during transformation of a system.

i.e., $-\Delta G = w_{net}$

It is also a state function; an extensive property and its differential is perfect.

G = H – TS

2.7.1.44. **Criteria for feasibility/spontaneity of a process:**

$\Delta Ssys + \Delta Ssur > 0$

The above criterion, however requires knowledge of both the ΔS_{sys} and ΔS_{sur} which is not convenient. Hence feasibility of a process can be explained from the change of other thermodynamics criteria.

$$dS = \frac{dq_{rev}}{T} = \frac{dU + PdV}{T}$$

So, for reversible process TdS = dU + PdV ......(i)

In the process occurs irreversibly, the heat absorbed will be less because $dq_{rev} > dq_{irr}$. So, TdS > dU + PdV............(ii)

Combining (i) and (ii)

$\boxed{TdS \geq dU + PdV}$......(iii) where equal to sign refers to a reversible process and greater than sign refers to an irreversible process.

Equation (iii) is the basic equation which leads to a number of criteria for predicting the feasibility of a process.

a) **Criterion in terms of entropy:**
   If internal energy and volume remain constant then dU = 0, dV = 0. Hence from eqn (iii) we have TdS $\geq$ 0.
   Or, $\boxed{dS_{U,V} \geq 0}$.

b) **Criterion in terms of internal energy:**
   If S & V are kept constant, then, dS = 0, dV = 0.
   From eqn (iii) $\boxed{dU_{S,V} \leq 0}$

c) **Criterion in terms of enthalpy:**
   If S is constant, then from eqn (iii) $\boxed{dH_{S,P} \leq 0}$

d) **Criterion in terms of change in Helmholtz free energy or work function:**
   By definition, work function (A), is given by
   A = U − TS
   Or, dA = dU − SdT − TdS
   Or, TdS = dU − SdT − dA
   Putting this in eqn (iii)
   dU − SdT − dA $\geq$ dU + PdV
   Or, - dA $\geq$ PdV + SdT
   Or, $\boxed{dA_{V,T} \leq 0}$

e) Criterion in terms of Gibbs free energy:

By definition, $G = H - TS = U + PV - TS$

Or, $dG = dU + PdV + VdP - TdS - SdT$

Or, $dU + PdV = dG - VdP + TdS + SdT$ ......(iv)

From eqn (iii) & (iv)

$TdS \geq dG - VdP + TdS + SdT$

Or, $\boxed{dG_{T,P} \leq 0}$

2.7.1.45. Some fundamental relations of thermodynamics:

From 1st law of thermodynamics

$dU = dq + dw$

For reversible process $dU = dq_{rev} - PdV$............(i)

Now $dS = \dfrac{dq_{rev}}{T}$ i.e., $dq_{rev} = TdS$.............(ii)

From, (i) and (ii) $\boxed{dU = TdS - PdV}$ ....(iii)

Again enthalpy, $H = U + PV$

Or, $dH = dU + PdV + VdP$

$\quad = TdS - PdV + PdV + VdP$

i.e., $\boxed{dH = TdS + VdP}$..........(iv)

Similarly, $\boxed{dA = -SdT - PdV}$..............(v)

And, $\boxed{dG = -SdT + VdP}$

2.7.1.46. Free energy change for isothermal expansion of ideal gas:

We know $dA = -SdT - PdV$

At constant temperature *whole eqn*

2.7.1.47. Gibbs-Helmholtz equation:

This equation represents the variation of A or G with temperature.

$$\Delta A = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1}$$

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$$

2.7.1.48. Maxwell's Relationship:

Maxwell deduced four relations which are widely used to simplify many mathematical problems in thermodynamics. To derive the relations, he used following relations

dU = TdS – PdV

dH = TdS + VdP

dA = –SdT – PdV

dG = – SdT + VdP

With proper derivatives, the four Maxwell's relation are

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

2.7.1.49. Chemical Potential and Standard Chemical Potential:

Chemical potential (μ) of a substance is the molar Gibbs free energy per mole of that substance.

So, $\mu = \bar{G} = \frac{G}{n}$

For any substance i in a mixture, the chemical potential (μ_i) is defined as the increase in Gibbs free per mole of the substance added keeping temperature, pressure and other mole numbers constant.

So, $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$

If the substance remains at standard state, then molar Gibbs free energy or partial molar Gibbs free energy is called standard chemical potential (μ^0).

$$\mu = \mu^0 + RT \ln P$$

2.7.1.50. Free energy change for isothermal mixing of ideal gases:

At constant temperature and pressure after mixing of i components, the free energy change will be, $\boxed{\Delta_{mix}G = nRT \sum x_i \ln x_i}$

2.7.1.51. **Clapeyron equation:**

Transition of state (i.e., melting, boiling, sublimation, allotropic transformation) occurs at a particular temperature at a given pressure. If pressure is changed transition temperature will also change. variation of transition temperature with pressure is given by an equation which is known as Clapeyron equation.

$$\frac{dP}{dT} = \frac{L_t}{T(V_2 - V_1)}$$

2.7.1.52. **Clausius Clapeyron equation:**

Clausius modified the Clapeyron equation for those cases where final phase is vapour i.e., for vaporization.

$\frac{dP}{P} = \frac{L_v}{R}\frac{dT}{T^2}$ [Differential form]

$$\ln\frac{P_2}{P_1} = \frac{L_V}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{L_V}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$ [Integrated form]

2.7.1.53. **Trouton's rule:**

the ratio of molar latent heat of vaporization and normal boiling point in kelvin scale is constant for a liquid i.e., molar entropy change during vaporization of a liquid is constant. This is known as Trouton's rule.

$\Delta S_v/mole$ = constant

This rule is not valid for associated liquid like H_2O, CH_3COOH etc.

according to this rule the entropy of vaporization for simple non associative liquid is 87.78 $J.k^{-1}$

2.7.1.54. **Kirchhoff's equation (influence of temperature on ΔH & ΔU):**

If a chemical change (or a physical change) occurs at more than one temperature, heat changes will be different. The relation between heat change and temperature is given by Kirchoff's equation.

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_P \, dT$$

$$\Delta U_2 = \Delta U_1 + \int_{T_1}^{T_2} \Delta C_V \, dT$$

2.7.1.55. **Laws of thermochemistry:**
  i.   Law of Lavoisier and Laplace.
  ii. Hess's law

2.7.1.56. **Law of Lavoisier and Laplace:**

This law states that heat change accompanying a chemical process in one direction is equal in magnitude but opposite in sign to that accompanying in the same reaction in the reverse direction.

2.7.1.57. **Hess's law:**

This law states that for a given chemical process then it heat change will be same whether the process occurs in one or in several steps.

2.7.1.58. Heat of neutralization of any strong acid and strong base is same (ΔH = -57.1 K.J). this is because all strong acids and bases are almost completely ionized. Therefore, heat of neutralization of a strong acid by a strong base or vice versa is actually heat of formation of one mole $H_2O(l)$ by the reaction of one mole H+ and one mole OH-.

2.7.1.59. **Third law of thermodynamics:**

At absolute zero every substance has a finite positive entropy main becomes zero and does so becomes in case of perfectly crystalline substances.
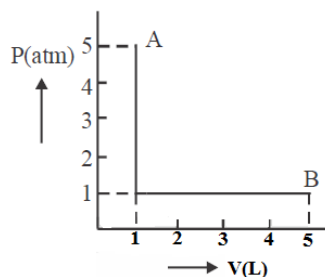
$$\lim_{T \to 0} \Delta S = 0$$

2.7.1.60. **Debye T³ law:**

This law states that the heat capacity depends on T³ near T = 0K.

$$T = 0, C_{V,m} = aT^3$$

Previous Year Solve

NET JUNE 2014

Q. The figure below represents the path followed by a gas during expansion from A→B. The work done is (L atm)

(a) 0   (b) 9   (c) 5   (d) 4

Ans.

As we know work, $W = P\Delta V$ $W = P(V_2 - V_1)$

$$\Rightarrow W = P(V_2 - V_1) + P\Delta V$$

$$= 5(1 - 1) + 1(5 - 1) \quad as \; \Delta V = V_2 - V_1 = 5 - 1$$

$$W = 1(4) = 4$$

Correct option is (d)

NET DEC 2014

Q. For a process in a closed system, temperature is equal to

(a) $\left(\frac{\partial H}{\partial P}\right)_S$ (b) $-\left(\frac{\partial A}{\partial V}\right)_T$ (c) $\left(\frac{\partial G}{\partial P}\right)_T$ (d) $\left(\frac{\partial H}{\partial S}\right)_P$

Ans. One of the fundamental equation of thermodynamics is

$$dH = TdS + VdP$$

Diff. both side with respect to S at constant P we get

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

Correct Option is (d).

NET JUNE 2015

Q.Heat capacity of a species is independent of temperature if it is

(a) tetratomic   (b) triatomic   (c) diatomic   (d) monatomic

Ans. For a monoatomic gas no vibrational degree of freedom is found, only translational degree of freedom is occurred.

Correct option is (d).

Q. Consider the progress of a system along the path shown in the figure $\Delta S(B \to C)$ for one mole of anideal gas is then given by
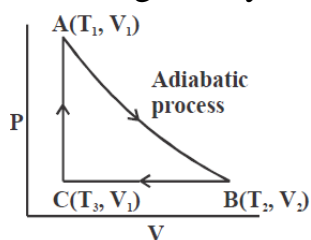
(a) $R \ln \frac{T_1}{T_3}$ (b) $R \ln \frac{T_3}{T_1}$ (c) $R \ln \frac{V_2}{V_1}$

(d) $R \ln \frac{V_1}{V_2}$

Ans.

As we know, $\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$

In this case, $\frac{T_2}{T_1} = \frac{T_3}{T_2}$ and $\frac{V_2}{V_1} = \frac{V_1}{V_2}$

Therefore, $\Delta S = C_v \ln \frac{T_3}{T_2} + R \ln \frac{V_1}{V_2}$

$\Rightarrow \Delta S = \int_{T_2}^{T_3} \frac{dV}{T} + \int_{T_2}^{T_3} \frac{PdV}{T}$

If, $C_v \ln \left(\frac{T_3}{T_2}\right) = 0$

Then, $(\Delta S)_{B \to C} = R \ln \frac{V_1}{V_2}$

Correct option (d)

NET DEC 2015

Q. The value of ΔU-ΔH for the reaction $Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$ is

(a) -3RT   (b) +3RT   (c) +RT   (d) -RT

**Ans.** As we know $\Delta H = \Delta U + \Delta n_g RT$ i.e., $\Delta H - \Delta U = \Delta n_g RT$

For the given chemical reaction, $Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$, $\Delta n_g = 3$

Correct Option is (b).

Q. If the pressure p (system) is greater than the p (surroundings), then

(a) work is done on the system by the surroundings

(b) work is done on the surroundings by the system

(c) work done on the system by the surroundings is equal to the work done on the surroundings by the system

(d) internal energy of the system increases

Ans. As the system pressure is greater than surrounding,
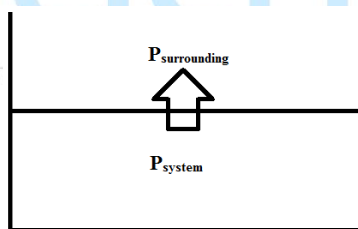
This means work done by the system on the surrounding.

Correct option is (b).

NET JUNE 2016

Q. $\left(\frac{\partial H}{\partial P}\right)_T$ has the dimension of

(a) pressure   (b) volume   (c) temperature   (d) heat capacity

Ans. $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$; it shows that $\left(\frac{\partial H}{\partial P}\right)_T$ has a parameter of V.

Correct option is (b).

Q.For an ideal gas at 300K

(a) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (b) $\left(\frac{\partial U}{\partial T}\right)_V = 0$ (c) $\left(\frac{\partial H}{\partial T}\right)_P = 0$ (d) $\left(\frac{\partial G}{\partial T}\right)_P = 0$

Ans. One of the Maxwell equation is

$dU = TdS - pdV$ ………..(i)

Differentiating equation (i) with respect to V at constant T we get,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_P - P$ as per thermodynamic relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_P$ ……..(ii)

For 1mol ideal gas, PV=RT, i.e., $P = \frac{RT}{V}$ putting this into equation (ii)
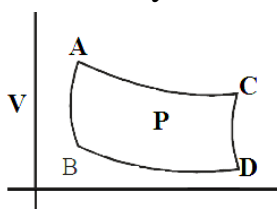
$$\left(\frac{\partial U}{\partial V}\right)_T = T\left\{\frac{\partial}{\partial T}\left(\frac{RT}{V}\right)\right\}_V - P$$

$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{V}\right) - P$

$= \frac{TR}{V} - P = \frac{TR}{RT/P} - P = P - P = 0$, as V=RT/P.

Correct option is (a).

Q.The figure below describes how a Carnot engine works. It starts from the adiabatic compressionstep denoted by

(a) AB   (b) BC   (c) DC   (d) AD

Ans. Only BC is adiabatic compression.

Correct option is (b)

Q. If U is a function of V and T, $\left(\frac{\partial U}{\partial T}\right)_P$ is equal to (π and α are the internal pressure and the coefficient of thermal expansion, respectively)

(a) C_P (b) C_V (c) $C_P - \pi V\alpha$ (d) $C_P - \pi V\alpha$

Ans.

Given, $U = f(T, V)$

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

Differentiating both sides with respect to T at constant P we get,

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

$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_P = C_V + \pi \left(\frac{\partial V}{\partial T}\right)_P$ as we know $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ and

Again, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ i.e., $\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$

Therefore, $\boxed{\left(\frac{\partial U}{\partial T}\right)_P = C_V + \pi\alpha V}$

Correct option is (d).

NET JUNE 2016

Q. The parameter which always decreases during a spontaneous process atconstant S and V, is

(a) U   (b) H   (c) C_P (d) q

Ans.

From Clausius inequality, $dS \geq \dfrac{dq}{T}$

$dS \geq \dfrac{dU + PdV}{T}$ as $dU = dq - PdV$

$\Rightarrow dU + PdV - TdS \leq 0$

Atconstant S and V, the above equation becomes

$$(dU)_{S,V} \leq 0$$

Correct option is (a).

Q. The equation of state for one mole of a gas is given by $P(V - b) = RT$, where b and R are constants. The value of $\left(\dfrac{\partial H}{\partial P}\right)_T$ is

(a) V-b   (b) b   (c) 0   (d) $\dfrac{RT}{P} + b$

Ans.

$dH = TdS + VdP$ ....(i)

Differentiating eqn. (i) with respect to P at constant T we get,

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Again, from Maxwell's relation $\left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$

So, $\left(\dfrac{\partial H}{\partial P}\right)_T = -T\left(\dfrac{\partial V}{\partial T}\right)_P + V$ ....(ii)

Now for the given gas equation, $P(V - b) = RT$, $PV - Pb = RT$.....(iii)

Differentiating eqn. (iii) with respect to T at constant P we get,

$$P\left(\frac{\partial V}{\partial T}\right)_P - 0 = R$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \text{.......(iv)}$$

Putting (iv) into (ii) we get,

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\frac{R}{P} + V \text{.....(v)}$$

Now from $P(V - b) = RT$, we get

$$(V - b) = \frac{RT}{P}$$

$$\Rightarrow -\frac{RT}{P} = -V + b$$

Putting the above value on (v) we get,

$$\left(\frac{\partial H}{\partial P}\right)_T = -V + b + V = b$$

Correct option is (b).

Q. The partial derivative $\left(\frac{\partial T}{\partial V}\right)_P$ is equal to

(a) $-\left(\frac{\partial P}{\partial S}\right)_T$ 　　(b) $-\left(\frac{\partial P}{\partial S}\right)_V$ 　　(c) $-\left(\frac{\partial P}{\partial S}\right)_n$ 　　(d) $-\left(\frac{\partial P}{\partial S}\right)_H$

Ans. $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ ....(i)

Now, according to reciprocal theorem of partial derivative

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial T/\partial V}\right)_T$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{1}{\partial P/\partial S}\right)_T$$

Putting the above value on (i) we get,

$$\left(\frac{1}{\partial V/\partial T}\right)_P = -\left(\frac{1}{\partial P/\partial S}\right)_T$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial S}\right)_T}$$

Correct option is (a).

NET JUNE 2017

Q. The correct statement for any cyclic thermodynamic process is

(a) $\oint dq = 0$ (b) $\oint dw = 0$ (c) $\oint dU = 0$ (d) $\oint V dq = 0$

Ans. As per thermodynamic criterion for any cyclic process the cyclic integral of state function is zero.

Correct option is (c).

NET DEC 2017

Q. Enthalpy is equal to

(a) $TS + PV + \sum u_i n_i$ (b) $TS + \sum u_i n_i$ (c) $\sum u_i n_i$ (d) $PV + \sum u_i n_i$

Ans. We know,

$$G = \sum u_i n_i$$

$$G = H - TS$$

$$H = G + TS$$

$$H = \sum u_i n_i + TS$$

Correct option is (b).

Q. In stretching of a rubber band,

$$dG = VdP - SdT + fdL$$

Which of the following relations is true?

(a) $\left(\dfrac{\partial S}{\partial L}\right)_{P,T} = -\left(\dfrac{\partial f}{\partial T}\right)_{P,L}$ (b) $\left(\dfrac{\partial S}{\partial L}\right)_{P,T} = -\left(\dfrac{\partial f}{\partial V}\right)_{P,L}$

(c) $\left(\dfrac{\partial S}{\partial L}\right)_{P,T} = -\left(\dfrac{\partial V}{\partial T}\right)_{P,L}$ (d) $\left(\dfrac{\partial S}{\partial L}\right)_{P,T} = -\left(\dfrac{\partial f}{\partial P}\right)_{T,L}$

Ans. $dG = VdP - SdT + fdL$ ……. (i)

Differentiating eqn. (i) with respect to T at constant P, L we get,

$$\left(\frac{\partial G}{\partial T}\right)_{P,L} = -S$$

Similarly, differentiating eqn. (i) with respect to L at constant P, T we get,

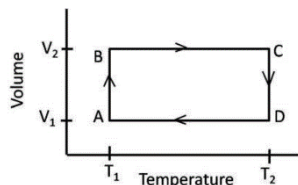$$\left(\frac{\partial G}{\partial L}\right)_{P,T} = f$$

As G is a state function

$$\left[\frac{\partial}{\partial L}\left(\frac{\partial G}{\partial T}\right)_{P,L}\right]_{T,P} = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial L}\right)_{T,P}\right]_{P,L}$$

$$\Rightarrow \left(\frac{\partial S}{\partial L}\right)_{P,T} = -\left(\frac{\partial f}{\partial T}\right)_{P,L}$$

Correct option is (a).

Q. One mole of an ideal gas undergoes a cyclicprocess (ABCDA) starting from point Athrough 4 reversible steps as shown in thefigure. Total work done inthe process is
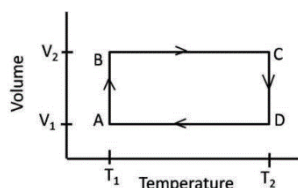

(a) $R(T_1 - T_2)\dfrac{V_2}{V_1}$
(b) $R(T_1 + T_2)\dfrac{V_2}{V_1}$

(c) $R(T_1 + T_2)\ln\dfrac{V_2}{V_1}$
(d) $R(T_1 - T_2)\ln\dfrac{V_2}{V_1}$

Ans.

$$w_{total} = w_{AB} + w_{BC} + w_{CD} + w_{DA}$$

Now, $w_{AB} = -nRT_1 \ln\dfrac{V_2}{V_1}$ [Isothermal work]

$w_{BC} = 0$ [as the process is isochoric, $\Delta V=0$]

$w_{CD} = -nRT_2 \ln\dfrac{V_1}{V_2} = nRT_2 \ln\dfrac{V_2}{V_1}$ [Isothermal work]

$w_{DA} = 0$ [as the process is isochoric, $\Delta V=0$]

Now,

$$w_{total} = w_{AB} + w_{BC} + w_{CD} + w_{DA}$$

$$= -nRT_1 \ln\frac{V_2}{V_1} + 0 + nRT_2 \ln\frac{V_2}{V_1} + 0$$

$$= R(T_1 - T_2) \ln\frac{V_2}{V_1}$$

Correct option is (d).

NET JUNE 2018

Q. At 300K, the thermal expansion coefficient and the isothermal compressibility of liquid water are $2 \times 10^4 K^{-1}$ and $5 \times 10^{-5} bar^{-1}$, respectively. $\left(\frac{\partial U}{\partial V}\right)_T$ (in kbar) for water at 320K and 1bar will be

(a) 2.4   (b) 1.2   (c) 0.6   (d) 12.0

Ans.

$\alpha = 2 \times 10^4 K^{-1}$ and $\beta = 5 \times 10^{-5} bar^{-1}$

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

$$\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V = \frac{2 \times 10^4}{5 \times 10^{-5}}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 320 \times 4 - 1 = 1279 bar = 1.279 \, kbar$$

Correct option is (b).