THERMODYNAMICS

MEASUREMENT OF ΔU and ΔH : Calorimetry

Heat Exchange at Constant Volume and Constant Pressure $(q_D and q_V)$

Heat exchange can be divided into two parts:



Hence heat exchanged at constant pressure and volume are important Definite quantities

Heat Capacity

The heat capacity of a system may be defined as the amount of heat required to raise the temperature of the system by one degree.

If δq is the small quantity of heat added to the system, let the temperature of the system rises by dT, then heat capacity C of the system is given by

$$C = \frac{dq}{dT}$$
(i)

In case of gases, we have two types of heat capacity i.e., heat capacity at constant volume and heat capacity at constant pressure.

Heat Capacity at Constant Volume(C_v)

Molar heat capacity at constant volume is defined by the relation

$$C_{\rm V} = \frac{\mathrm{d}q_{\rm v}}{\mathrm{d}T} \qquad \dots (\mathrm{i}\mathrm{i})$$

For first law of thermodynamics

But

dw = P dV $\therefore \qquad dU = dq - P dV \qquad \dots(iii)$

dU = dq - dw

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At constant volume

 $dU = dq_v$

 \therefore Heat capacity at constant volume C_v is given by

$$C_{\mathbf{V}} = \frac{\mathrm{d}q_{\mathbf{v}}}{\mathrm{d}T} = \left(\frac{\partial U}{\partial T}\right)_{\mathbf{v}}$$
$$C_{\mathbf{V}} = \left(\frac{\partial U}{\partial T}\right)_{\mathbf{v}} \qquad \dots (\mathrm{i}\mathbf{v})$$

or

It may be defined as the rate of change of internal energy with temperature at constant volume.

Heat Capacity at Constant Pressure (C_p)

When pressure is maintained constant, equation (i) takes the form

$$C_{P} = \frac{\delta q_{v}}{dT} \qquad \dots (v)$$

From first law of thermodynamics

At constant pressure

$$\delta q_p = (dU + PdV) = dH$$

[$\Theta H = U + PV$ At constant P, dH = dU + PdV]
 $\therefore \quad \delta q_p = dH \qquad \dots(vi)$

Heat capacity at constant pressure C_p is given by

$$C_{p} = \frac{\delta d_{p}}{dT} = \left(\frac{\partial H}{\partial T}\right)_{p}$$
$$C_{p} = \left(\frac{\partial H}{\partial T}\right)_{p} \qquad \dots (vii)$$

or

It is the rate of change of enthalpy with temperature at constant pressure.

Hence heat capacity of a system at constant volume C_V is equal to the increase in internal

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energy of the system per degree rise of temperature at constant volume. Similarly heat capacity at constant pressure C_p is numerically equally to the increase in enthalpy of the system per degree rise of temperature.

For one mole of gas $C_p - C_v = R$

For 'n' moles of gas $C_p - C_v = nR$

Degree of Freedom and Equipartition Principle

Degree of Freedom is defined as the total number of modes on which a molecule of an ideal gas exchange energy during collisions. If a molecule contains only one atom (as in a monatomic gas), it has three degrees of freedom corresponding to translational motion in the three independent spatial directions X, Y and Z.



vibrational degree of freedom can be calculated by the following method

$$f_v = 3N - (f_t + f_r)$$

Table shows that the observed values of for diatomic molecules deviate greatly from the predicted values, The fact that the value of 5 cal deg⁻¹ mol⁻¹(which is close to 5R/2) is most common for simple diatomic molecules shows that vibration degrees of freedom are active only at very high temperature. The following graph shows



Variation of heat capacity at constant volume of a diatomic gas due to excitation of rotational and vibrational levels.

variation of C_V with temperature highlighting the fact that with increase in temperature the vibration modes of motion also contribute to the heat capacity According to Law of equipartition of energy.

- (i) each translation and rotational degree of freedom in a molecule contributes $\frac{1}{2}$ RT to the thermal energy of one mole of a gas,
- (ii) each vibrational degree of freedom in a molecule contributes RT to the thermal energy of one mole of a gas.

Isochoric and Isobaric Process

An isochoric process, also called a constant-volume process, an isovolumetric process, or an isometric process, is a thermodynamic process during which the volume of the closed system undergoing such a process remains constant.

Volume is constant throughout the process.

$$dV = 0$$

W = $\int -P.dV = 0$
from first law of thermodynamics
 $\Delta U = q + W$
 $\Delta U = qV = nCV\Delta T$

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An isobaric process is a thermodynamic process in which the pressure stays constant: ? P = 0. The term derives from the Greek iso- (equal) and baros (weight). The heat transferred to the system does work, but also changes the internal energy of the system. ... Since pressure is constant, this means that.

Pressure is constant

 $W = -P_{ext}(V_2 - V_1)$

from first law of thermodynamics

 $\Delta U = q + W$

at constant P, $\Delta U = q_P - P(V_2 - V_1)$

 $q_P = \Delta U + P(V_2 - V_1) = \Delta H$



Relationship Between $\rm C_p$ and $\rm C_v$ for Ideal Gas

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

from the first law dH = dU + d(PV) for a differential change in state

if only ideal gas is involved PV=nRT $dU=nC_VdT$ and $dH=nC_pdT$

substituting these results, we get

 $nC_{p}dT = nC_{V}dT + nRdT$

 $C_p = C_v + R$ valid only for ideal gas

relationship between C_p and C_v for real gases, liquid and solids is beyond the scope of JEE syllabus.

Isothermal processes can be further classified into two types - Reversible & Irreversible.

Analysis of Different Thermodynamic Processes

ISOTHERMAL PROCESS

Reversible Isothermal Process

If the gas is expanded from initial volume V_1 to final volume V_2 by gradually changing external pressure infinite steps, process is called reversible isothermal process.



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During reversible process:

$$P_{ext} = P_{int} \pm dP$$

$$\Rightarrow P_{ext} = P_{int} = \frac{nRT}{V}$$
 for an ideal gas

because
$$P_{int} = P_{ideal} = \frac{nRT}{V}$$

dw_{rev, isothermal} = - PdV

$$\int dw = -\int \frac{nRT}{V} dV$$

Work done in reversible isothermal expansion

$$\mathbf{w} = -\mathbf{n}\mathbf{R}\mathbf{T}\ln\left(\frac{\mathbf{V}_2}{\mathbf{V}_1}\right)$$

ADIABATIC PROCESS

In thermodynamics, an adiabatic process is one that occurs without transfer of heat or matter between a thermodynamic system and its surroundings. In an adiabatic process, energy is transferred only as work.



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Reversible Adiabatic Process: In an adiabatic process, no loss or gain of heat takes place i.e.,

 $dq = 0. ext{From first law, we have,}$ dq = dU + dwSince dq = 0 $\therefore ext{ } dU = -dw$ For an ideal gas, $dU = C_V dT$ $\therefore ext{ } C_V dT = -dw = -pdV$ or, $C_V dT = -(nRT/V)dV$

or,
$$C_V dT/T + nR dV/V = 0$$

Integrating the above equation between T_1 and T_2 and V_1 and V_2 , the initial and final temperature and volumes, we have,

$$\int_{T_1}^{T_2} C_v \frac{\partial T}{T} + nR \int_{V_1}^{V_2} \frac{\partial V}{V} = 0$$
$$\frac{T_2}{C_v \ln} \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = 0$$

Λ	r
υ	L

$$C_{v} \ln \frac{T_{2}}{T_{1}} = -nR \ln \frac{V_{2}}{V_{1}} \implies \ln \frac{V_{2}}{V_{1}} = \ln \left(\frac{T_{2}}{T_{1}}\right)^{\frac{-C_{v}}{nR}}$$

$$\ln \frac{V_{2}}{V_{1}} = \ln \left(\frac{T_{2}}{T_{1}}\right)^{\frac{-1}{\gamma-1}} (\Theta C_{V} = \frac{nR}{\gamma-1})$$

$$\frac{V_{2}}{V_{1}} = \left(\frac{T_{2}}{T_{1}}\right)^{\frac{-1}{\gamma-1}} = \left(\frac{T_{1}}{T_{2}}\right)^{\frac{1}{\gamma-1}}$$

$$\left(\frac{V_{2}}{V_{1}}\right)^{\gamma-1} = \left(\frac{T_{1}}{T_{2}}\right)^{\frac{-1}{\gamma-1}} = (1)$$
.....(1)

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Or
$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$$

T. $V^{\gamma - 1} = \text{constant}$

For an ideal gas,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$
$$\frac{T_1}{T_2} = \frac{P_1 V_1}{P_2 V_2}$$
.....(2)

or

 \therefore from equation (1) & (2) we have

 ${\tt P}_1{\tt V}_1{}^\gamma={\tt P}_2{\tt V}_2{}^\gamma=\text{constant}$

In general, for a reversible adiabatic expansion

P.
$$V^{\gamma} = \text{constant}$$
 Applicable only on a
 $TV^{\gamma - 1} = \text{constant}$ reversible adiabatic process
 $TP^{1 - \gamma/\gamma} = \text{constant}$
 $\Theta q = 0$
 $\Rightarrow W = \Delta U = nC_V (T_2 - T_1)$
 $= nR \frac{(T_2 - T_1)}{\gamma - 1}$
 $= \frac{nRT_2 - nRT_1}{\gamma - 1}$
 $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$

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Irreversible Adiabatic Process: Suppose an ideal gas is confined in a adiabatic container fitted with friction less piston. If the thermodynamic equilibrium of system is disturbed by changing external pressure suddenly by finite value and let the system come to equilibrium the process is irreversible adiabatic process. The work done (w) is given by

$$\Delta U = w = -P_{ext} (V_f - V_i)$$

$$\Delta U = nC_V (T_f - T_i)$$

$$\Rightarrow nC_V (T_f - T_i) = -P_{ext} (V_f - V_i)$$

$$nC_V (T_f - T_i) = -P_{ext} \left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)$$

First we have to calculate the final temperature (T_f) from this equation.

noww =
$$\Delta U$$
 = nC_V (T₂ - T₁)
w = $\left[\frac{P_{f}V_{f} - P_{i}V_{i}}{\gamma - 1}\right]$

Comparison of Isothermal and Adiabatic Process

Starting from same state, if system is allowed to expand to same final pressure,

|w_{rev}, isothermal|>|w_{rev}, adiabatic|.

In reversible isothermal process, heat is entering from surrounding, while in adiabatic process, work is done on the expansion of internal energy of system.

Starting from same initial state, if system is compressed to same final pressure, $w_{rev, adia} > w_{rev, iso}$. During adiabatic compression, the work done is getting stored in the system, and temperature of system increses, the gas become less and less compressible, and greater work is required to compress the system.

POLYTROPIC PROCESS

A process described by $PV^{X} = C$ is called polytropic process, where x is a real number.



Work done for polytropic process:

dw = -PdV

Let us suppose an ideal gas is undergoing polytropic process

$$dw = -PdV$$

$$\int dw = \int_{V_1}^{V_2} \frac{C}{V^n} dV$$

$$W = \begin{bmatrix} \frac{-C}{(-n+1)} \cdot \frac{1}{V_1^{n-1}} \end{bmatrix}_{V_1}^{V_2}$$

$$\Rightarrow \frac{C}{(n-1)} \cdot \left(\frac{1}{V_2^{n-1}} - \frac{1}{V_1^{n-1}} \right)$$

$$w = \frac{C}{(n-1)} \left(\frac{P_2 V_2 - P_1 V_1}{C} \right)$$

$$W = \left(\frac{P_2 V_2}{n} \right)$$

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Heat Capacity (C_m) For Polytropic Process

 ${\tt T}\,.\,{\tt V}^{n-1}={\rm constant}$

On differentiating we get

substituting (iii) in equation (ii)

$$C = n_g C_V + \frac{n_g R}{1 - n}$$

from 1 mole gas

$$C = C_v + \frac{R}{1-n}$$

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Relationship Between $\Delta_r H$ and $\Delta_r U$ in Chemical Reactions:

For a general chemical reaction given by

$$aA + bB ---> cC + dD$$

 $\Theta H = U + PV$
 $\Delta H = \Delta U + \Delta (PV)$

if P is constant then

$$\Delta_r H = \Delta_r U + P(\Delta V)$$

$$\Delta_r H = \Delta_r U + P(V_f - V_i) \qquad (2)$$

(a) If all the reactant and products are ideal gases V_c , V_d , V_a and V_b all are equal to molar volume of ideal gas e.g. V = RT/P which on substitution in previous equation gives

Where Δn_g is difference of stoichiometric coefficient of gaseous products and gaseous reactants.

- (b) In case of liquid and solids present in chemical equations, their molar volumes can be ignored in comparison to molar volume of ideal gases and hence do not count stoichiometric coefficient of solid and liquids in Δn_g .
- (c) In case of non-ideal behaviour of gases, equation (2) should be used.