

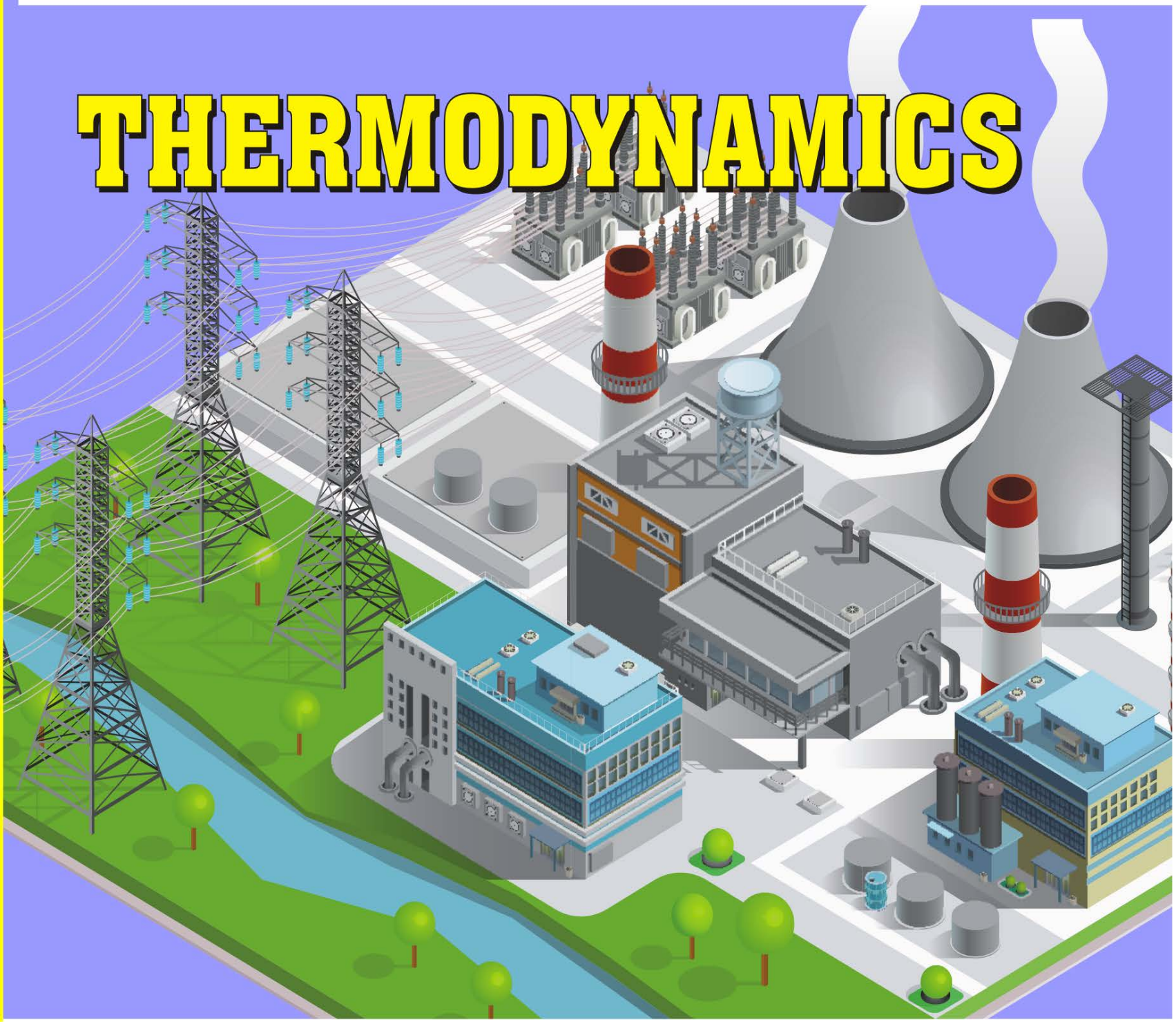


India's Best Institute for CHEMICAL ENGINEERING

CHEMICAL ENGINEERING

REVISED AS PER GATE

THERMODYNAMICS





CHEMICAL ENGINEERING

REVISED AS PER NEW GATE Syllabus

STUDY MATERIAL

THERMODYNAMICS

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GATE-2024 Thermodynamics Syllabus

First and Second laws of thermodynamics. Applications of first law to close and open systems. Second law and Entropy. Thermodynamic properties of pure substances: Equation of State and residual properties, properties of mixtures: partial molar properties, fugacity, excess properties and activity coefficients; phase equilibria: predicting VLE of systems; chemical reaction equilibrium.

Thermodynamics : Marking Analysis in GATE (2010 to 2024)

Year	1 Mark	2 Marks	Total Marks
2024	1 × 1	2 × 3	7
2023	1 × 3	2 × 3	9
2022	1 × 4	2 × 3	10
2021	1 × 2	2 × 4	10
2020	1 × 2	2 × 6	14
2019	1 × 4	2 × 4	12
2018	1 × 3	2 × 5	13
2017	1 × 3	2 × 4	11
2016	1 × 3	2 × 3	9
2015	1 × 4	2 × 4	12
2014	1 × 4	2 × 3	10
2013	1 × 2	2 × 5	12
2012	1 × 2	2 × 4	10
2011	1 × 2	2 × 3	8
2010	1 × 1	2 × 4	9

List of Topics in GATE 2024 paper from Thermodynamics

Partial molar properties, First law, Residual property, Carnot engine.












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and many more

Chapter-1

INTRODUCTION

The word “Thermodynamics” originates from Therme (means heat) + dynamic (means force). The subject is concerned with the interrelation between energy and change of state of any real world system. Thermodynamics forms the basis for the study of a vast variety of devices such as refrigerators, air conditioners, aircraft, power plant etc, the application of which is involved in the everyday life of almost every individual. Every thermodynamics equipment / device makes use of a working substance on which the processes are executed. Most commonly utilized working substances are water and air. H₂O is the working substance in steam power plant; air is the working substance in petrol and diesel engines, etc. The subject of thermal sciences deals with relations between the relevant properties of working substances, energy interactions and inter conversions in the form of ‘work’ and ‘heat’. It is the science of relations between heat, work and the properties of the system.

Thermodynamic system: It is defined as a quantity of matter or region in space chosen for study. For the purpose of thermodynamic analysis, it is necessary to define a ‘system’

Surrounding: The mass or region outside the system is said to be the surrounding. For all practical purposes, in any thermodynamic analysis of a system it is necessary to include only the immediate surroundings in which the effects are felt.

Boundary: The real or imaginary surface that separates the system from its surroundings. It may change in shape as well as in size over time, i.e., increase or decrease

Universe: A system and its surrounding together comprise a universe

Q. 1 How does one characterize the changes that occur in the system during any thermodynamic process?

Ans. This can be done if one could measure the change in terms of some properties of the system.

A thermodynamic system is, thus, characterized by its properties, which are the descriptors of state of system.

1.1. Some important concepts about system:

Properties of system

The descriptive characteristic of a system are called its properties such as pressure P, temperature T, volume V, mass m and moles n. Properties are supposed to be either intensive or extensive. Intensive properties are those that are independent of the mass or numbers of moles of the system e.g. temperature, pressure and density. Extensive properties are those whose value depends on the size of the system (mass or moles) e.g. total mass, total volume, etc. The ratio of two extensive properties of a homogeneous system is called intensive property. e.g. specific volume. If an extensive property is divided by the mass or number of moles of a substance forming a system, then intensive property is called a specific property or molar property respectively e.g. specific volume, molar volume, etc.

Molar properties are denoted by \bar{V} , \bar{H} , etc.

Specific properties are denoted by v, h, etc.

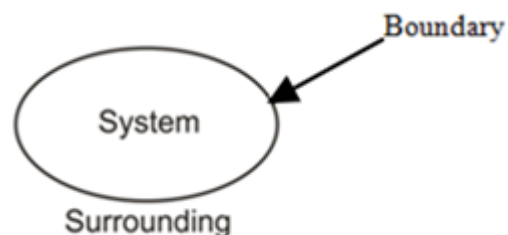


Fig.1.1. Thermodynamic system

$$v = \frac{V}{m}, \quad \bar{V} = \frac{V}{n}$$

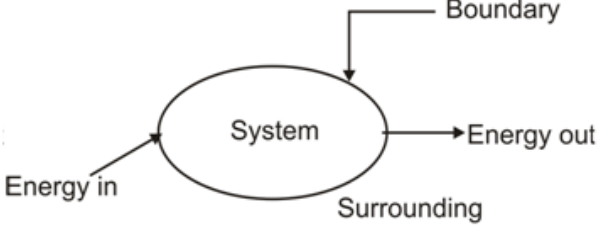
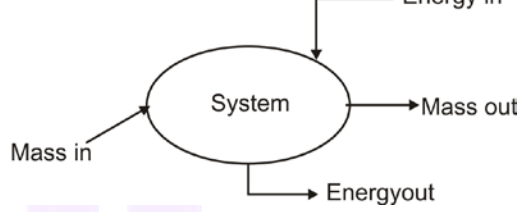
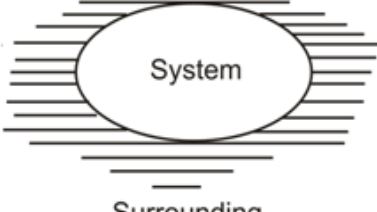
Specific gravity is defined as the ratio of density of the substance to that of standard or reference substance (air is taken as reference substance of gases and water for liquid).

Mass density (also known as simple density) is the ratio of change of mass with volume, also known as specific density. It is the reciprocal of specific volume.

Molar density is defined in a similar manner and is reciprocal of molar volume.

Classes of system

- (a) Closed system
- (b) Open system
- (c) Isolated system

<p>Closed system: It is a system of fixed mass. There is energy transfer (i.e. heat or work can cross the system boundary) but no mass transfer can occur across the system boundary. e.g. A certain quantity of fluid in a cylinder bounded by a piston.</p>	 <p style="text-align: center;">Fig.1.2. Closed system</p>
<p>Open system: A system in which mass and energy crosses the boundary of the system. e.g. An air compressor in which air enters at low pressure and leaves at high pressure</p>	 <p style="text-align: center;">Fig.1.3. Open system</p>
<p>Isolated system: It is one in which there is no interactions between the system and the surroundings. Hence neither mass transfer nor energy transfer take place across the system boundary.</p>	 <p style="text-align: center;">Fig.1.4. Isolated system</p>

Homogeneous and Heterogeneous system:

Phase: A quantity of matter homogeneous throughout in chemical composition and physical structure is said to be phase. viz, solid, liquid and gas

Homogeneous system: A system including of single phase is called homogenous system.

Heterogeneous system: A system consisting of more than one phases is said to be a heterogeneous system.

1.2. Thermodynamic Properties, processes and cycles:

Thermodynamic Equilibrium: A system is known to exist in a state of thermodynamic Equilibrium when no change in any macroscopic property is registered, when the system is isolated from its surroundings. Change of state of a thermodynamic system results from existence of gradients of various types within or across its boundary. Temperature gradient results in heat transfer, velocity gradient results in momentum transfer, concentration gradient results in mass transfer. As long as these gradients exist, system will undergo a change of state. The result of all such changes is to nullify the gradients. The ultimate limit where all gradients are non – existent and system undergoes no further changes is the ‘**state of thermodynamic Equilibrium**’. For a system in thermodynamic Equilibrium, it needs to also satisfy the criteria for mechanical, chemical and thermal Equilibrium.

State: When all the properties (pressure, volume, temperature) of a system have definite values, the system is known to be at a definite state. Fig. 1.5.shows two different states of a thermodynamic system.

Path: The succession of states passed through at the time of a change of state is said to be the path of the change of state.

Process: When the path is fully specified, the change of state is known as process. e.g. constant pressure process, constant volume process or any change that a system undergoes from one Equilibrium state to another is called a process

Cycle: As a series of state changes such that the final state is identical with initial state. As shown in fig.1.6. “a-b” is a process and “1-2-1” is a cycle.

Thus in a cyclic process, initials states coincides with the final state.

Mechanical Equilibrium: Absence of any unbalanced force within the system itself and between the surroundings and the system.

Chemical Equilibrium: If its chemical composition does not change with time, i.e. no chemical reaction happen.

Thermal Equilibrium: When there is no spontaneous change in any property of the system.

Quasi–static process: A quasi–static process is one which occurs in such a way that changes in one part does not occur faster than other part of the system. Hence, the deviation from thermodynamic Equilibrium is very small. All states of the system passes through are Equilibrium states. In the system (as shown in fig.1.7.), if the weights are removed slowly, one at a time, and the system is allowed to come to Equilibrium after every removal of weight, the

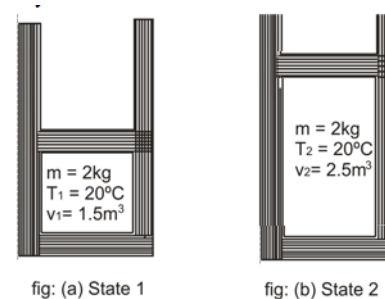


fig: (a) State 1

fig: (b) State 2

Fig. 1.5. Diagrammatic representation of two states of a system

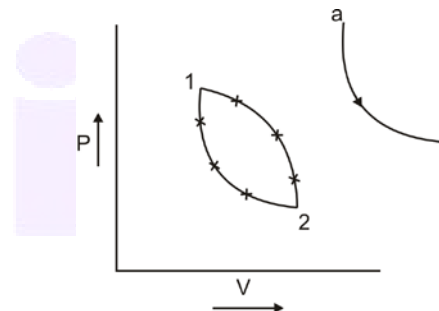


Fig.1.6. Pictorial representation of a cyclic process

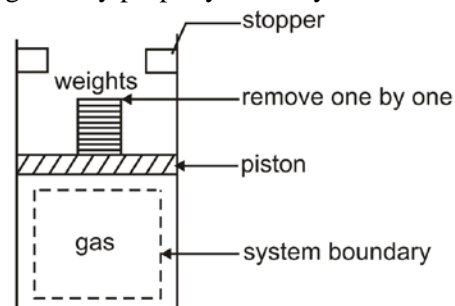


Fig.1.7. Carrying out a Quasi-Equilibrium process on a gas by removal of weights in infinitesimal steps

Questions and Solutions

1. Convert the following readings of pressure to kPa, assuming that the barometer reads 760 mm of Hg.

- (a) 40 cm Hg vacuum
- (b) 90 cm Hg gauge
- (c) 1.2 m of H₂O gauge

Solution:

$$(a) P_{\text{vacuum}} = h\rho g = (40 \times 10^{-2}) \times (13.6 \times 10^3) \times 9.8 \\ = 53.31 \times 10^3 \text{ N/m}^2 = 53.31 \text{ kPa}$$

$$P_{\text{absolute}} = P_{\text{atm}} - P_{\text{vacuum}} \\ = (760 - 400) \times 9.8 \times 13.6 \times 10^3 \\ = 48 \times 10^3 \text{ N/m}^2 = 48 \text{ kPa}$$

$$(b) P_{\text{gauge}} = h\rho g = (90 \times 10^{-2}) \times (13.6 \times 10^3) \times 9.8 \\ = 120 \times 10^3 \text{ N/m}^2 = 120 \text{ kPa}$$

$$\text{Since } P_{\text{atm}} = 760 \text{ mm Hg} = 101.325 \text{ kPa}$$

$$P_{\text{absolute}} = P_{\text{gauge}} + P_{\text{atm}} \\ = 120 + 101.325 = 221.325 \text{ kPa}$$

$$(c) P_{\text{gauge}} = h\rho g = 1.2 \times 1000 \times 9.81 \\ = 11.772 \text{ kPa}$$

$$P_{\text{absolute}} = 11.772 + 101.325 = 113.097 \text{ kPa}$$

2. Acceleration is sometimes measured in g's, or multiples of the standard acceleration of gravity. Determine the net upward force that an astronaut whose mass is 68 kg experiences if the acceleration on lift-off is 10 g's.

Solution:

Net vertical force

$$F_{\text{net}} = F = mg = ma$$

$$A = 10 \times 9.806 = 98.06 \text{ m/s}^2$$

$$F = 68 \times 98.06 = 6668 \text{ N}$$

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Chapter-2

WORK AND HEAT TRANSFER

Types of energies associated with thermodynamic processes: A thermodynamic system containing a fluid possess both potential energy and kinetic energy which constitute macroscopic, mechanical forms of energy. Another is the microscopic forms of energy which is due to

- Translation, Rotation and vibration of atoms/ molecules (INTRAMOLECULAR)
- INTERMOLECULAR interactions
- Motion, spin of electrons, nucleus – electron or nucleus – nucleus interactions (INTRATOMIC)

The energy possessed by matter due to the microscopic modes of motion is referred to as the internal energy of matter. Thus, when a thermodynamic system undergoes change of state, the change in internal energy is responsible for the energy leaving or entering the system. This exchange is done by heat or work. A closed system and surrounding can interact in following ways:

(a) By work transfer

(b) By heat transfer

If work is done by the system, it is taken to be positive and when is done upon the system, it is taken negative.

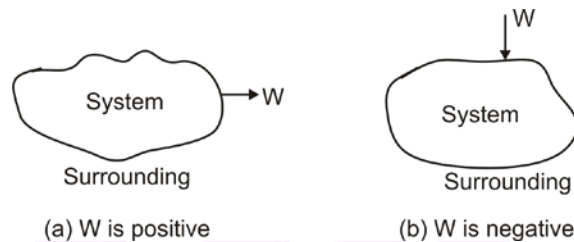


Fig. 2.1. Sign convention for work used in thermodynamics

2.1. PdV Work or Displacement Work:

Work refers to a form of energy transfer which results due to changes in external macroscopic physical constraints on a thermodynamic system. Mechanical work is most commonly encountered in real thermodynamic systems. Such work results from the energy applied to expand the volume of the system against an external pressure. Force is applied on the system boundary due to which it either contracts or expands. Consider gas in the cylinder (as shown in fig.2.2.) be a system. Initial pressure P_1 and volume V_1 . The system is in thermodynamic Equilibrium, the state of which is denoted by the coordinate's P_1, V_1 .

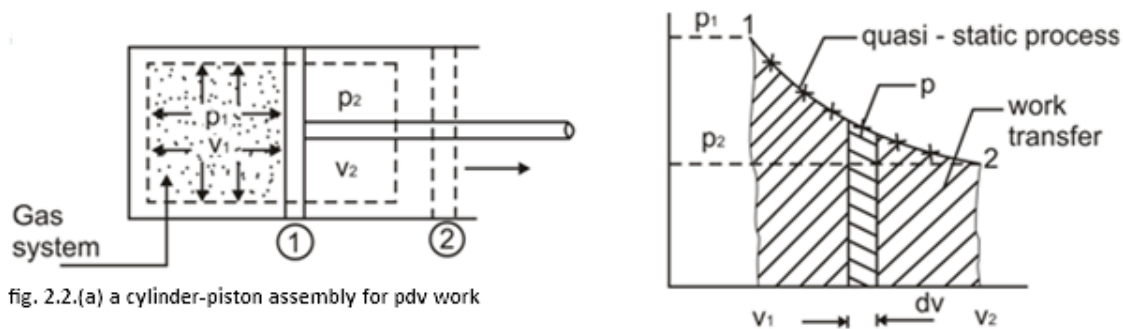


fig. 2.2.(a) a cylinder-piston assembly for pdv work

fig.2.2.(b) graphical representation of pdv work

Fig.2.2. Diagrammatic representation of PdV work

The piston is the only boundary which moves because of gas pressure. Suppose the piston move out to final position 2. This new position is also a thermodynamic Equilibrium state described by P_2, V_2 . Any intermediate point in the travel of the piston, pressure is P and volume V . If the piston moves an infinitesimal distance dl and if 'a' be the area of the piston, then force F acting on the piston is given by $F=P.a$. The infinitesimal amount of work done by the gas on the piston

$$\delta W = F.dl = P.adl = PdV \text{ [If piston area } a \text{ is constant]}$$

Hence, we can say that when work is done by the system (EXPANSION), volume increases and work done is positive. The reverse is true when work is done on the system (COMPRESSION), volume decreases and hence work done is negative. If the piston moves out from state 1 to state 2 with volume changing from V_1 to V_2 . The amount of work w done by

$${}_1W_2 = \int_{V_1}^{V_2} PdV$$

The integration $\int PdV$ can be performed only on a quasi-static path. Work is path function and δW is an inexact or imperfect differential. Thermodynamic properties are point function i.e. there is definite value for each property. For cyclic process, the change in any property is zero

$$\oint dV = 0, \oint dP = 0, \oint dT = 0$$

Where \oint stands for the cyclic integral for the closed path.

2.2. Heat

Heat is that form of energy that is exchanged between system and its surrounding owing to a temperature differential between the two. Heat always flows down the gradient of temperature. Heat flow is regarded to be positive for a thermodynamic system, if it enters the system and negative if it leaves. Like work, heat is a form of energy that exists only in transit between a system and its surrounding. So after transit, both work and heat can only transform into the kinetic and potential energy of the constituent atoms and molecules. Like work, SI unit of heat is also Joule (J). But in common use and general applications, calorie is used. In some applications Btu is the prescribed unit of heat given by

British Thermal Unit (Btu) $\Rightarrow 1\text{Btu} = 252\text{cal}$

$1/180^{\text{th}}$ quantity of heat which when transferred to one pound mass of water raised its temperature from 32°F (ICE POINT) to 212°F (STEAM POINT) at standard atmosphere pressure.

Similarly calories is defined as $1/100^{\text{th}}$ quantity of heat which when transferred to one kilogram mass of water raised its temperature from 0°C to 100°C at standard atmospheric pressure.

Relation between Temperature scales

- 1) $T(^{\circ}\text{C}) = T(\text{K}) - 273.15$
- 2) $T(\text{R}) = 1.8T(\text{K})$
- 3) $T(^{\circ}\text{F}) = T(\text{R}) - 459.67$
- 4) $T(^{\circ}\text{F}) = 1.8 T(^{\circ}\text{C}) + 32$

2.3. Laws of Thermodynamics:

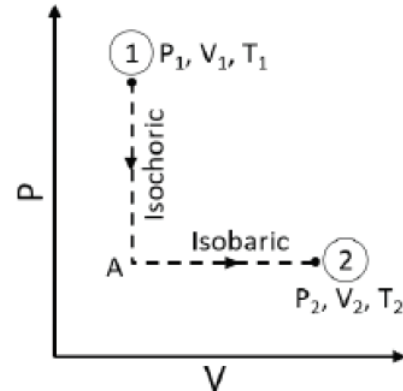
The extent of change of state of system due to transfer of energy to or from the system is captured through the basic equations of thermodynamics which are derived starting from a set of fundamental observations known as "Laws of thermodynamics". The laws are the postulates that govern the nature of interaction of real systems and energy. These are human observations to which no exceptions have been found so far and so are considered to be "Laws". The laws are applicable from microscopic to macroscopic order.

$$W_s = (\Delta H)_S = \int_{P_1}^{P_2} V dP \quad (\text{Assumption is that } V \text{ is independent of } P)$$

$$W_s = V(P_2 - P_1)$$

Questions and solutions

1. N moles of an undergo a two-step process as shown in the figure. Let P, V and T denote the pressure, volume and temperature of the gas, respectively. The gas, initially at state-1 (P_1, V_1, T_1), undergoes an isochoric (constant volume) process to reach state-A, and then undergoes an isobaric (constant pressure) expansion to reach state-2 (P_2, V_2, T_2). For an ideal gas, $C_p - C_v = NR$, where C_p and C_v are the heat capacities at constant pressure and constant volume, respectively, and assumed to be temperature independent. The heat gained by the gas in the two-step process is given by



(GATE-2022 : 2-Makrs)

- (A) $P_2V_2 - P_1V_1$ (B) $P_2(V_2 - V_1) + C_p(T_2 - T_1)$
 (C) $P_2(V_2 - V_1) + C_v(T_2 - T_1)$ (D) $C_p(T_2 - T_1) + C_v(T_2 - T_1)$

Answer: c

Example:

Assuming at point A, and $T = T'$ $V = V_1$

For isochoric process

$$W = 0, Q_1 = C_v(T' - T_1)$$

For isobaric process

$$W = P_2(V_2 - V_1)$$

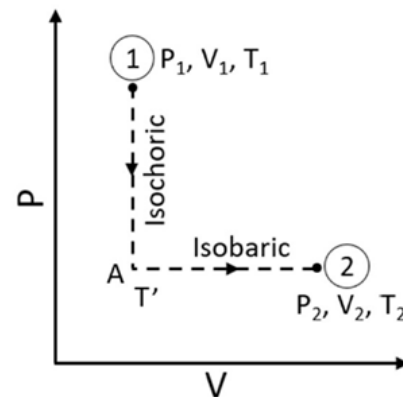
$$U = C_v(T_2 - T')$$

$$Q_2 = U + W = P_2(V_2 - V_1) + C_v(T_2 - T')$$

$$\text{Total heat gain} = Q_1 + Q_2$$

$$= C_v(T' - T_1) + P_2(V_2 - V_1) + C_v(T_2 - T')$$

$$Q = P_2(V_2 - V_1) + C_v(T_2 - T_1)$$



2. Water flows over a waterfall 200 m in height. Take 2 kg of the water as the system, and assume that it does not exchange energy with its surroundings.

- (a) What is the potential energy of the water at the top of the falls with respect to the base of the falls?
 (b) What is the kinetic energy of water just before it strikes bottom?

Solution:

- (a) Potential energy of the water

Chapter-3

Second Law of Thermodynamics

Need of second law of thermodynamics

The first law provides a constraint on the total energy contained in a system and surroundings. However, it provides no constraint on the possible direction a process may take place. However, in the real world such constraints do exist. Spontaneous processes in nature happen in one direction. Heat always flows from a body at a high temperature to a body at a lower temperature, water always flows downward, time always flows in the forward direction. e.g.



cup of hot coffee left in a cooler room eventually cools off. Further, it is observed that work is readily transformed into other forms of energy (including heat). But is impossible to develop a device that may work in a continuous manner and convert heat completely into work or any other form of energy. Second law of thermodynamic is formulated to answer these 2 questions:

- 1) Direction of heat transfer?
- 2) What determines the efficiency of conversion of heat to work?

The second law of thermodynamics is utilized in calculating the theoretical limits for the performance of commonly used engineering systems e.g heat engines and refrigerators

Thermal energy reservoir:

It is defined as a large body of infinite heat capacity, which is capable of rejecting or absorbing unlimited quantity of heat without suffering appreciable changes in its thermodynamic coordinates. In practice, large bodies of water e.g oceans, lakes and rivers as well as atmospheric air. The atmosphere does not warm up as a result of heat losses from residential buildings in winter.

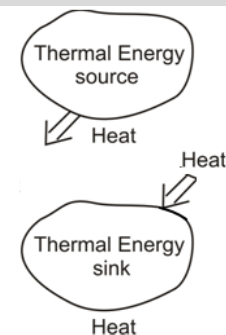


Fig.3.1. Diagrammatic representation of source and sink

Source: A reservoir that supplies energy in the form of heat is known as source.

Sink: A reservoir that absorbs energy in the form of heat is said to be sink.

3.1.Heat Engine

It is a thermodynamic cycle in which there is net heat transfer, to the system and a net work transfer (W_{net}) from the system. The system which executes a heat engine cycle is known as heat engine. All that engines absorb heat at a higher temperature body (source) and release a fraction of it to a low temperature body (sink), the difference between the two quantities constitutes the net work delivered during the cycle. Heat Q_1 is transferred from the furnace to the water in the boiler to form vapour.

Then works on the turbine rotor to produce work. Steam is condensed to H₂O in the condenser in which an amount of heat is rejected from the system, and eventually work (W_p) is done on the system to pump it to the boiler and system repeats the cycle the net heat transfer (Q_{net}) in cycle.

$$Q_{net} = Q_1 - Q_2$$

The net work transfer in a cycle

$$W_{net} = W_T - W_P$$

According to the first law of thermodynamics

$$\sum_{cycle} Q = \sum_{cycle} W$$

$$Q_{net} = W_{net}$$

$$Q_1 - Q_2 = W_T - W_P$$

Block diagram of cyclic heat engine, indicating the various energy interactions. Boiler, turbine, condenser and pump all four together constitute a heat engine. The efficiency of a heat engine or heat engine cyclic is

$$\eta = \frac{\text{Net work output of the cycle}}{\text{Total heat input to the cycle}} = \frac{W_{net}}{Q_1}$$

$$\eta = \frac{W_{net}}{Q_1} = \frac{W_T - W_P}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$\boxed{\eta = 1 - \frac{Q_2}{Q_1}}$$

3.2. Heat Pump

The device that transfer of heat from a low – temperature medium to a high – temperature one is the heat pump. “It is a device which, operating in a cycle, maintains a body, say A, at a higher temperature than the temperature of surroundings. Heat pump and refrigerator operate on the same cycle but differ in their objectives. The objective of a heat pump, is to maintain a heated space at a higher temperature. Coefficient of performance (COP)_{HP}, is defined as:

$$(COP)_{HP} = \frac{\text{desired output}}{\text{required input}} = \frac{Q_1}{W_{net}}$$

$$\boxed{(COP)_{HP} = \frac{Q_1}{Q_1 - Q_2}}$$

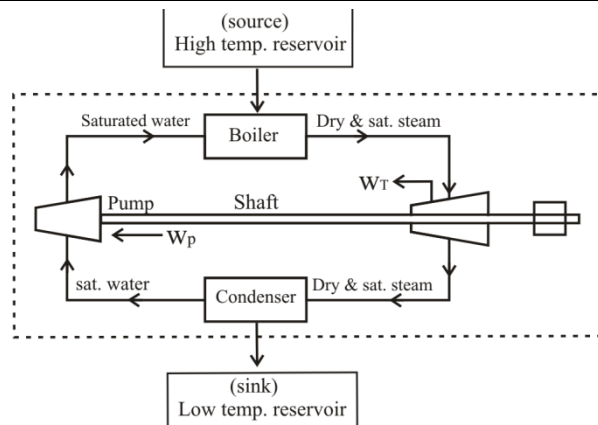
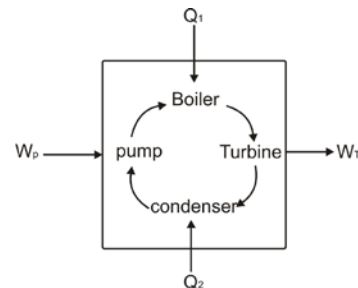


Fig. 3.2. Schematic diagram of a heat engine



[As per 1st law of thermodynamics $Q_{net} = W_{net}$]

Questions and solution

Q.1 Consider a system where a Carnot engine is operating between a source and a sink. Which of the following statements about this system is/are NOT correct?

- (A) This engine is reversible.
 (B) The engine efficiency is independent of the source and sink temperatures.
 (C) This engine has the highest efficiency among all engines that operate between the same source and sink.
 (D) The total entropy of this system increases at the completion of each cycle of the engine.

Answer: B & D

(GATE-2023 : 1-Mark)

For option-B

⇒ For Carnot engine

$$\eta = \frac{W_{\text{net}}}{Q_1} = 1 + \frac{T_2 \ln(P_C / P_D)}{T_1 \ln(P_A / P_B)}$$

$$\text{or } \eta = \frac{W_{\text{net}}}{Q_1} = 1 - \frac{T_2}{T_1} \quad \text{thus } \eta = f(T_1, T_2)$$

For option-D

As Carnot engine follows cyclic operation, thus entropy, a state function, will be constant.

- 2.** A cyclic heat engine operates between a source temperature of 800°C and a sink temperature of 30°C. What is the least rate of heat rejection per kW net output of the engine?

Solution

For a reversible engine, the rate of heat rejection will be minimum

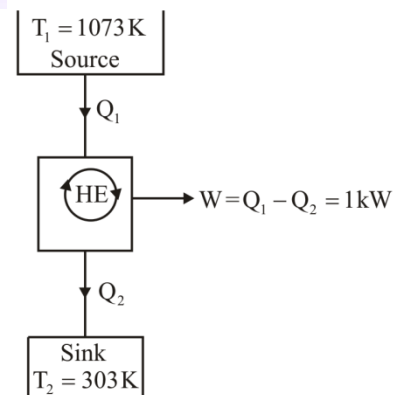
$$\eta_{\text{max}} = \eta_{\text{rev}} = 1 - \frac{T_2}{T_1}$$

$$= 1 - \frac{30 + 273}{800 + 273} = 1 - 0.282 = 0.718$$

$$\text{Now, } \frac{W_{\text{net}}}{Q_1} = \eta_{\text{max}} = 0.718$$

$$\therefore Q_1 = \frac{1}{0.718} = 1.392 \text{ kW}$$

$$\text{Now, } Q_2 = Q_1 - W_{\text{net}} = 1.392 - 1 = 0.392 \text{ kW}$$



- 3.** It is required to freeze 1 kg water at 273 K by means of a refrigeration machine which operates in the surroundings at 300 K. The latent heat of fusion of ice at 273 K is 334.11 kJ/kg. Determine
- (a) The minimum amount of work required
 (b) The heat given up the surroundings

Solution

The work required will be minimum for an ideal Carnot machine acting as a refrigerator. The coefficient of performance (COP) of such a machine is given by the relation

$$COP = \frac{Q_2}{W} = \frac{T_2}{T_1 - T_2} \quad \dots(1)$$

Here, Q_2 is the heat absorbed at a temperature T_2 , and T_1 is the temperature of the surroundings to which heat is given up. For freezing 1 kg water, the heat to be removed is 334.11 kJ, i.e. $Q_2 = 334.11$ kJ.

(a) From equation (1)

$$W = \frac{Q_2(T_1 - T_2)}{T_2} = 334.11 \frac{300 - 273}{273} = 33.04 \text{ kJ}$$

(b) Since $W = Q_1 - Q_2$,

$$Q_1 = W + Q_2 = 33.04 + 334.11 = 367.15 \text{ kJ}$$

4. A domestic food freezer maintains a temperature of -15°C . The ambient air temperature is 30°C . If heat leaks into the freezer at the continuous rate of 1.75 kJ/s what is the least power necessary to pump this heat out continuously?

Solution

Freezer temperature, $T_2 = 15 + 273 = 258 \text{ K}$

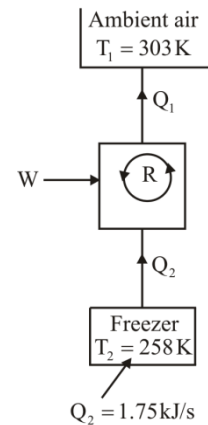
Ambient air temperature, $T_1 = 30 + 273 = 303 \text{ K}$

The refrigerator cycle removes heat from the freezer at the same rate at which heat leaks into it (fig)

For minimum power $\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$

$$\therefore Q_1 = \frac{1.75}{2.8} \times 303 = 2.06 \text{ kJ/s}$$

$$\therefore W = Q_1 - Q_2 = 2.06 - 1.75 = 0.31 \text{ kJ/s} = 0.31 \text{ kW}$$



5. A refrigerated space is maintain at -14°C (259.15K) and cooling water is available at 19°C (292.15K) refrigeration capacity is 40 kW. The evaporator and condenser are to sufficient size that minimum temperature difference 6°C (6K) for heat transfer can be realized in each case. Calculate coefficient of performance for a Carnot refrigerator.

Solution: Coefficient of performance (ω) = $\frac{T_C}{T_H - T_C}$

$$\omega = \frac{(259.15 - 6)}{(292.15 - 6) - (259.15 - 16)}$$

$$\omega = 7.67$$

Hence coefficient of performance for a Carnot refrigerator is 7.67

6. Calculate ΔU and ΔH for 1kg of water when it is vaporized at the constant temperature of 100°C (373.15 K) and the constant pressure of 101.325 kPa. Specific volumes of liquid and vapour water at these conditions are 0.00104 and $1.673 \text{ m}^3\text{kg}^{-1}$. For this change, heat in the amount of 2256.9 kJ is added to water.

Chapter-6

Solution Thermodynamics

Application of Thermodynamics to Gas mixtures and Liquid solutions

Chemical Potential of species i in the mixture is given by $\mu_i = \left[\frac{\partial(\eta G)}{\partial n_i} \right]_{P, T, n_j}$ Where n_j indicate that all

mole number except the n_i are held constant. n is the total number of moles of the system, G is the total Gibbs free energy. For any closed system $nG = f(P, T)$. For an open system, material may pass into and out of the system and nG becomes a function of number of moles of chemical species present, i.e. $nG = g(P, T, n_1, n_2, \dots, n_i, \dots)$

Fundamental property relation for single phase fluid system of variable mass and composition is given by

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i dn_i$$

It is the foundation upon which the structure of solution thermodynamics is built. For the special case of one mole of solution, $n = 1$ and $n_i = x_i$:

$$dG = VdP - SdT + \sum \mu_i dx_i$$

$$V = \left(\frac{\partial G}{\partial P} \right)_{T, x} \quad \text{and} \quad S = - \left(\frac{\partial G}{\partial T} \right)_{P, x}$$

Gibbs free energy, when expressed as a function of its canonical variables, implicitly represents complete property information and other thermodynamic properties can be calculated from it by using simple

mathematical operations. e.g. $H = G + TS$, $H = G - T \left(\frac{\partial G}{\partial T} \right)_{P, x}$

Key point regarding chemical potential: Multiple phases at same T and P are in Equilibrium when chemical potential of each species is same in all phases.

$$\text{i.e. } \mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi$$

$$(i = 1, 2, \dots, N)$$

Here, π represents the no. of phases and N is the number of species present in the system.

6.1. Partial Property

We define partial molar property \bar{M}_i of species i in solution as $\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i} \right]_{P, T, n_j}$, Where \bar{M}_i may

be partial molar internal energy (\bar{U}_i) partial molar enthalpy (\bar{H}_i), partial molar entropy (\bar{S}_i), partial molar Gibbs energy (\bar{G}_i). When n is replaced by m (mass), this equation yields partial specific properties

rather than partial molar properties. Here, M are the solution properties and \bar{M}_i are the partial properties. In addition, properties of the individual species as they exist in pure state and T and P of the solution are represented by M_i and are called pure species properties. It can be proved that chemical potential and the

partial molar Gibbs energy are identical. Hence $\mu_i = \bar{G}_i$

Following equation is used to calculate mixture or solution property from partial property:

$$M = \sum_i x_i \bar{M}_i \quad \dots(1)$$

Or

$$nM = \sum_i n_i \bar{M}_i$$

where M stands for molar internal energy U, molar enthalpy H, molar entropy S, molar Gibbs energy G. Gibbs-Duhem equation is given by:

$$\left(\frac{\partial M}{\partial P} \right)_{T,x} dp + \left(\frac{\partial M}{\partial T} \right)_{p,x} dT - \sum_i x_i d\bar{M}_i = 0$$

This equation must be satisfied for all changes in P, T and \bar{M}_i caused by changes of state in a homogenous phase. At constant T and P Gibbs-Duhem equation becomes:

$$\sum_i x_i d\bar{M}_i = 0$$

Partial Property in Binary Solution

For binary solution equation (1) become

$$M = x_1 \bar{M}_1 + x_2 \bar{M}_2$$

Differentiation of this equation gives

$$dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 + \bar{M}_2 dx_2$$

When M is function of x_1 at constant T and P.

$$[x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0]$$

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1} = M - x_2 \frac{dM}{dx_2}$$

$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

Hence for binary system, the partial properties are calculated directly from an expression for the solution property as a function of composition at constant T and P. The corresponding equations for multicomponent systems are much more complex.

Important: For every equation that provides a linear relation among thermodynamic properties of a constant composition solution, there is a counterpart equation which connects the corresponding partial properties of each species in the solution

Eg. $H = U + PV$

For n moles

$$nH = nU + P(nV)$$

Differentiation w.r.t n_i at constant T, P and n_j

Questions and solutions

Q.1: Water in a container at 290 K is exposed to air containing 3 % CO₂ by volume. Air behaves like an ideal gas and is maintained at 100 kPa pressure. The liquid phase comprising of dissolved CO₂ in water behaves like an ideal solution. Use Henry's constant of CO₂ dissolved in water at 290 K as 12 MPa. Under equilibrium conditions, which one of the following is the **CORRECT** value of the mole fraction of CO₂ dissolved in water?

- (A) 2.9×10^{-4} (B) 0.9×10^{-4} **(GATE-2023 : 2-Marks)**
 (C) 2.5×10^{-4} (D) 0.5×10^{-4}

Answer : C

From Henry law

$$\bar{p}_i = x_i K_i \text{ (Henry Lay)} \quad \dots(1)$$

$$\text{A/s } \bar{p}_i = y_i p \text{ (Raoult 's Law)} \quad \dots(2)$$

From (1) & (2)

$$y_i P = x_i K_i$$

Given, $y_i = 3\% = 0.03$ $P = 100 \text{ kPa}$ $K_i = 12 \text{ MPa}$ $x_i = ?$

$$\therefore 0.03 \times 100 \times 10^3 = x \times 12 \times 10^6$$

$$\Rightarrow x = 2.5 \times 10^{-4}$$

Q.2: The enthalpy (H, in J.mol⁻¹) of a binary liquid system at constant temperature and pressure is given as

$$H = 40x_1 + 60x_2 + x_1x_2(4x_1 + 2x_2),$$

where x_1 and x_2 represent the mole fractions of species 1 and 2 in the liquid, respectively. Which one of the following is the **CORRECT** value of the partial molar enthalpy of species 1 at infinite dilution, \bar{H}_1^∞ (in J.mol⁻¹)? **(GATE-2023 : 2-Marks)**

- (A) 100 (B) 42 (C) 64 (D) 40

Answer: B

Sp. 1 at infinity dilution

$$\therefore \boxed{x_1 = 0}, \boxed{x_2 = 1}$$

By partial property diffusion

$$\bar{H}_1 = H - x_2 \frac{dH}{dx_2}$$

or $\bar{H}_1 = H + (1 - x_1) \frac{dH}{dx_1} = H + x_2 \frac{dH}{dx_1} \quad \dots(1)$ (As, $x_1 + x_2 = 1 \quad \therefore dx_1 = -dx_2$)

Given,

$$\begin{aligned}
 H &= 40x_1 + 60x_2 + x_1x_2(4x_1 + 2x_2) \\
 &= 40x_1 + 60(1-x_1) + x_1(1-x_1) \\
 &\quad [4x_1 + 2(1-x_1)] \\
 &= -20x_1 + 60 + 2x_1 - 2x_1^3 \quad \dots 2 \\
 \therefore \frac{dH}{dx_1} &= -20 + 2 - 6x_1^2 \\
 &= -18 - 6x_1^2 \quad \dots (3)
 \end{aligned}$$

Put equation (2) and (3) in equation (1)

$$\begin{aligned}
 \bar{H}_1 &= -20x_1 + 60 + 2x_1 - 2x_1^3 + x_2(-18 - 6x_1^2) \\
 \text{at } \bar{H}_1^\infty &= 60 - 18 = 42 \quad x_1 = 0 \\
 &\quad x_2 = 1
 \end{aligned}$$

Q.3 The molar excess Gibbs free energy (g^E) of a liquid mixture of A and B is given by

$$\frac{g^E}{RT} = x_A x_B [C_1 + C_2(x_A - x_B)]$$

Where, x_A and x_B are the mole fraction of A and B, respectively, the universal gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, T is the temperature in K, and C_1, C_2 are temperature-dependent parameters. At 300 K, $C_1 = 0.45$ and $C_2 = -0.018$. If γ_A and γ_B are the activity coefficients of A and B, respectively, the value of

$$\int_0^1 \ln \left(\frac{\gamma_A}{\gamma_B} \right) dx_A \quad \text{(GATE-2022 : 2-Marks)}$$

at 300 K and 1 bar is _____ (rounded off to the nearest integer).

Answer: 0

Example:

$$\frac{G^E}{RT} = X_A X_B [C_1 + C_2(X_A - X_B)] \quad \dots (1)$$

$$C_1 = 0.45 \quad C_2 = 0.018$$

$$\text{We know that } \frac{G^E}{RT} = X_A \ln \gamma_A + X_B \ln \gamma_B$$

$$\frac{G^E}{RT} = X_A \ln \gamma_A + (1 - X_A) \ln \gamma_B$$

$$\frac{\partial}{\partial X_A} \left(\frac{G^E}{RT} \right) = \ln \frac{\gamma_A}{\gamma_B} = \frac{\partial}{\partial X_A} [X_A(1 - X_A)(C_1 + C_2(2X_A - 1))]$$

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