Chemical Thermodynamics

First law

Recommended books

1. P. W. Atkins and J. D. Paula: Physical Chemistry (10th edition)
2. Ira N. Levine: Physical Chemistry (6th edition)

Lecture-1

Contents

- Chemistry/Physical Chemistry
- Areas of Physical Chemistry
- Roles of Physical Chemistry
- Applications of Physical Chemistry

Chemistry/Physical Chemistry

Chemistry is the science of composition and structure of materials and of the changes that materials undergo.

Physical Chemistry is the branch of chemistry that establishes and develops the principles of the subject in terms of the underlying concept of physics and the language of mathematics.

-P. W. Atkins

Physical chemistry is the study of the underlying physical principles that govern the properties and behavior of chemical systems.

-Levine

Areas of Physical Chemistry

- Thermodynamics
- Quantum chemistry
- Statistical mechanics
- Kinetics

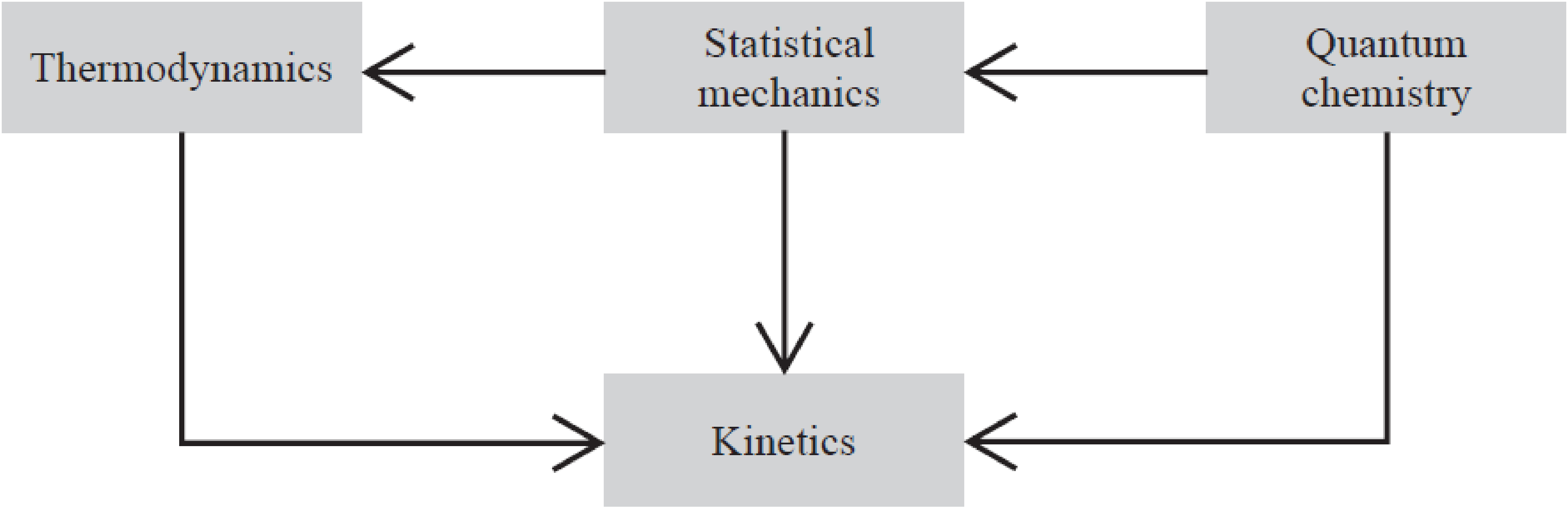
Thermodynamics is the study of the relationship between heat and other form of energy involved in a chemical or physical process.

Molecules and the electrons and nuclei that compose them do not obey classical mechanics. Instead, their motions are governed by the laws of quantum mechanics.

Quantum chemistry is a branch of chemistry focused on the application of quantum mechanics to chemical systems.

The molecular and macroscopic levels are related to each other by the branch of science called **statistical mechanics**. Statistical mechanics gives insight into why the laws of thermodynamics hold and allows calculation of macroscopic thermodynamic properties from molecular properties.

Kinetics is the study of rate processes such as chemical reactions, diffusion, and the flow of charge in an electrochemical cell. Kinetics uses relevant portions of thermodynamics, quantum chemistry, and statistical mechanics.



Thermodynamics

Statistical mechanics

Quantum chemistry

Kinetics

Roles of Physical chemistry

✓It provides the basis for developing new spectroscopic techniques and their interpretation, for understanding the structures of molecules and the details of their electron distributions for relating the bulk properties of matter to their constituent atoms.

✓Physical chemistry also provides a window on to the world of chemical reactions and allows us to understand in detail how they take place.

✓In fact, the subject strengthens the whole of chemistry, providing the principles to understand structure and change and providing the basis of all techniques of investigation.

Applications of Physical chemistry

The principles of physical chemistry provide a framework for all branches of chemistry.

Organic chemists use

- kinetics studies to figure out the mechanisms of reactions,
- quantum-chemistry calculations to study the structures and stabilities of reaction intermediates,
- symmetry rules deduced from quantum chemistry to predict the course of many reactions,
- nuclear-magnetic-resonance (NMR) and infrared spectroscopy to help determine the structure of compounds.

- **Inorganic chemists** use quantum chemistry and spectroscopy to study bonding.
- Analytical chemists use spectroscopy to analyze samples.

Biochemists use

- kinetics to study rates of enzyme catalyzed reactions;
- thermodynamics to study biological energy transformations, osmosis, and membrane equilibrium, and to determine molecular weights of biological molecules;
- spectroscopy to study processes at the molecular level (for example, intramolecular motions in proteins are studied using NMR); and
- x-ray diffraction to determine the structures of proteins and nucleic acids.

Environmental chemists use

- thermodynamics to find the equilibrium composition of lakes and streams,
- chemical kinetics to study the reactions of pollutants in the atmosphere, and
- physical kinetics to study the rate of dispersion of pollutants in the environment.

Chemical engineers use

- thermodynamics to predict the equilibrium composition of reaction mixtures, use kinetics to calculate how fast products will be formed, and
- principles of thermodynamic phase equilibria to design separation procedures such as fractional distillation.

Geochemists use thermodynamic phase diagrams to understand processes in the earth.

Polymer chemists use thermodynamics, kinetics, and statistical mechanics to investigate the kinetics of polymerization, the molecular weights of polymers, the flow of polymer solutions, and the distribution of conformations of a polymer molecule.

Lecture-2

Contents

- Thermodynamics
- Scopes of thermodynamics
- Basic Definitions
- State of a system
- State functions and path functions

Thermodynamics

Thermodynamics is the study of the relationship between heat and other form of energy involved in a chemical or physical process.

In a broader sense, thermodynamics studies the relationships between the macroscopic properties of a system.

The science which deals with the macroscopic properties of matter is known as classical thermodynamics. Here, the entire formulation can be developed without the knowledge that matter consists of atoms and molecules.

Equilibrium thermodynamics deals with systems in equilibrium. Irreversible thermodynamics deals with nonequilibrium systems and rate processes.

The term “thermodynamics” always mean equilibrium thermodynamics.

Statistical thermodynamics is another branch of science which is based on statistical mechanics and which deals with the calculation of thermodynamic properties of matter from the classical or quantum mechanical behavior of a large congregation of atoms or molecules.

Scope of thermodynamics

1. Most of the important laws of Physical Chemistry, including the van’t Hoff law of lowering of vapour pressure, Phase Rule and the Distribution Law, can be derived from the laws of thermodynamics.
2. It tells whether a particular physical or chemical change can occur under a given set of conditions of temperature, pressure and concentration.
3. It also helps in predicting how far a physical or chemical change can proceed, until the equilibrium conditions are established.

Limitations of thermodynamics

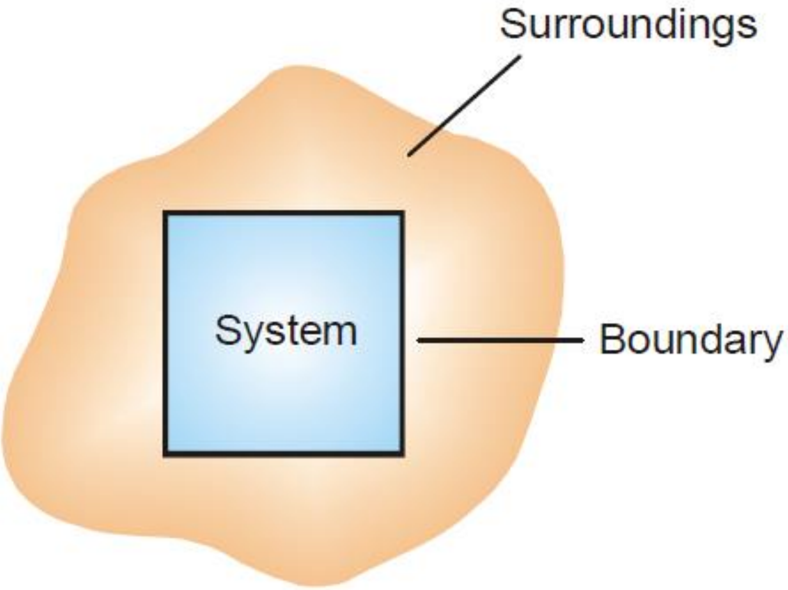
1. Classical thermodynamics is applicable to macroscopic systems consisting of matter in bulk and not to microscopic systems of individual atoms or molecules. It ignores the internal structure of atoms and molecules.
2. Thermodynamics does not bother about the time factor. That is, it does not tell anything regarding the rate of a physical change or a chemical reaction. It is concerned only with the initial and the final states of the system.

Basic Definitions

System: The system is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on.

Surroundings: The surroundings comprise the region outside the system and where we make our measurements.

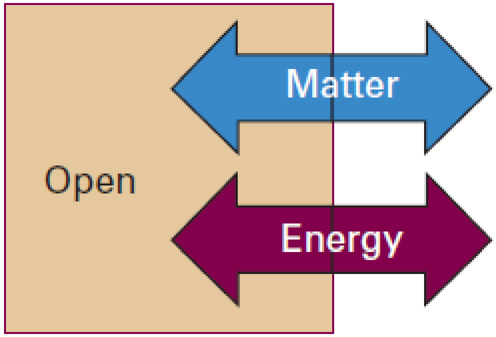
Boundary: The real or imaginary surface separating the system from the surroundings is called the boundary.



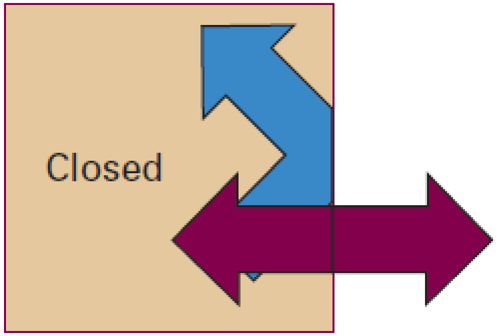
Basic Definitions

Types of System: The type of system depends on the characteristics of the boundary that divides it from the surroundings.

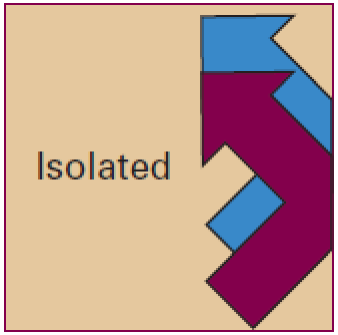
Open System: If both matter and energy can be transferred through the boundary between the system and its surroundings the system is classified as open.

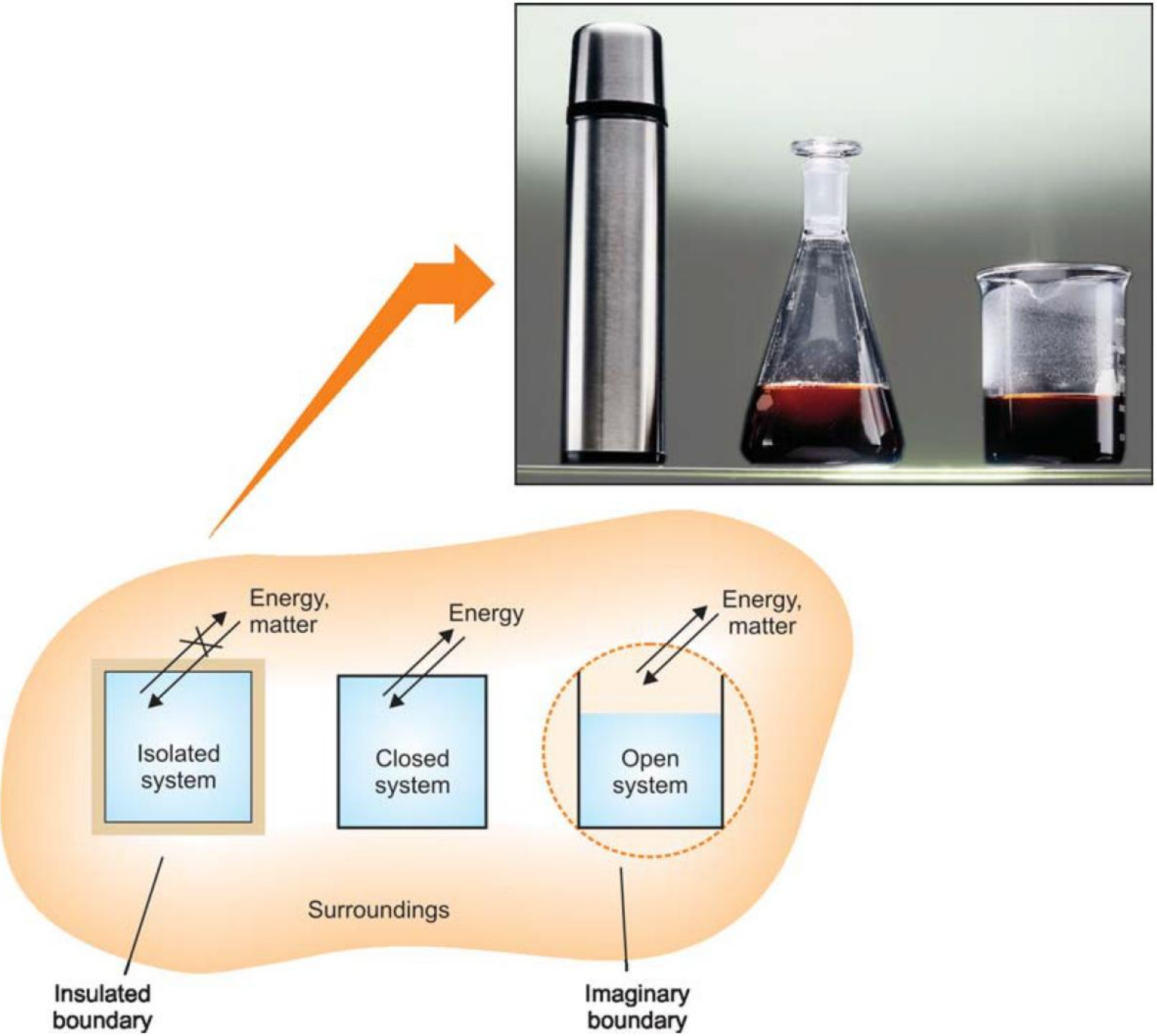


Closed System: If only energy pass through the boundary the system is classified as closed.



Isolated System: An isolated system is a thermodynamic system that cannot exchange either energy or matter outside the boundaries of the system.




Energy,
matter
Energy
Energy,
matter
Isolated
system
Closed
system
Open
system
Surroundings
Insulated
boundary
Imaginary
boundary

STATE OF A SYSTEM

A thermodynamic system is said to be in a certain state when all its properties are fixed.

The fundamental properties which determine the state of a system are pressure (P), temperature (T), volume (V), mass and composition.

State variables

The state of a system is defined by ascribing values to a sufficient number of state variables. Such variables are macroscopic properties such as pressure, volume, temperature, mass, composition, surface area etc.

In order to define a system completely, we need to state the values of only three variables, namely, P, V and T. The value of other variables will be definite and need not be stated.

STATE VARIABLES

It is not necessary to state all the properties (state variables) to define a system completely.

$PV = nRT$

Equation of state

If of the four state variables (n, P, V, T), n, P and T are specified, the value of fourth (V) is fixed automatically and can be calculated from the equation of state.

Dependent and Independent Variables

The variables (P and T) which must be necessarily specified to define the state of a system, are designated as **Independent state variables.** The remaining state variable is called Dependent state variable.

State Functions

In the thermodynamics of equilibrium, a state function for a thermodynamic system is a mathematical function relating several state variables that depend only on the current equilibrium thermodynamic state of the system not the path which the system has taken to reach its present state.

Path Functions

Physical quantities that depend on the path between two states are called path functions.

The two most common path functions are heat and work. The energy transferred as work or heat relates to the path being taken between states, not the current state itself.

Path Functions

Illustration

Suppose, a person may decide to hike up a 500 ft mountain. Regardless of what path the person takes, the starting place and the final place on top of the mountain will remain constant. The person may decide to go straight up to the mountain or decide to spiral around to the top of the mountain. There are many different ways to get to the final state, but the final state will remain the same.

State Variables Versus State Function

- State variable is something that we take as independent variable.
- State function is something that depends on previously selected state variables.

$$PV = nRT$$

Lecture-3

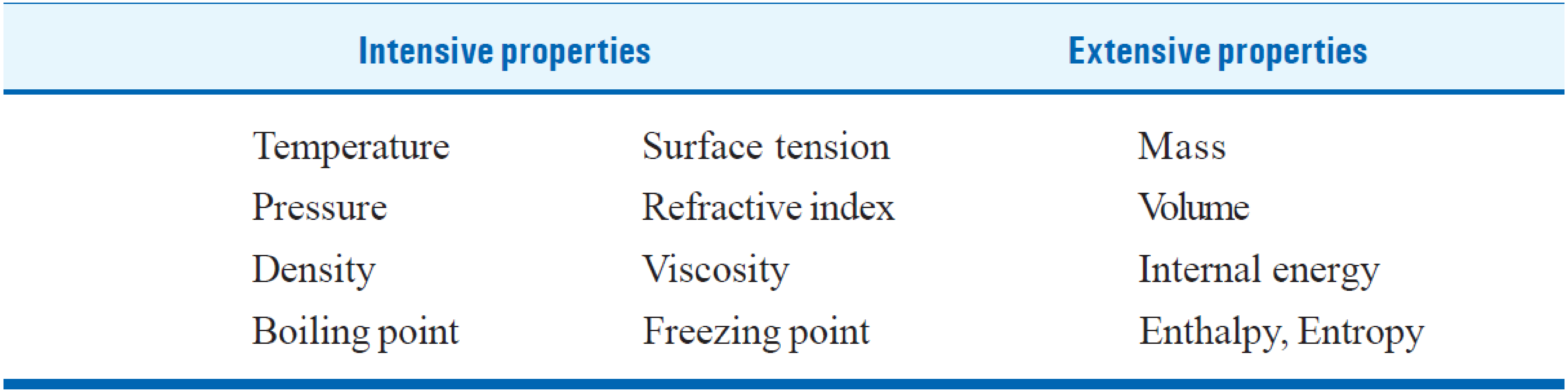
Contents

- Thermodynamic properties
- Intensive and extensive properties
- Thermodynamic processes
- Sample Questions

Intensive and Extensive Properties

- An extensive property is one whose value is equal to the sum of its values for the parts of the system. Thus, if we divide a system into parts, the mass of the system is the sum of the masses of the parts; mass is an extensive property. So is volume. Example of extensive properties: Volume, energy, heat capacity, enthalpy, entropy, free energy, length and mass.
- Properties that do not depend on the amount of matter in the system are called intensive. Examples of intensive properties/variables - temperature, pressure, concentration, density, dipole moment, refractive index, viscosity, surface tension, gas constant, sp. heat capacity, dielectric constant etc.

Intensive and Extensive Properties



Intensive properties		Extensive properties
Temperature	Surface tension	Mass
Pressure	Refractive index	Volume
Density	Viscosity	Internal energy
Boiling point	Freezing point	Enthalpy, Entropy

Thermodynamic Process

A process is the path along which a change of state takes place. A process is named according to the variety of conditions under which it occurs.

Isothermal process: This occurs under constant temperature condition. For an isothermal process $dT = 0$

Isobaric process: This occurs under constant pressure condition. For an isobaric process $dp = 0$

Isochoric process: This occurs under constant volume condition. For isochoric processes $dV = 0$.

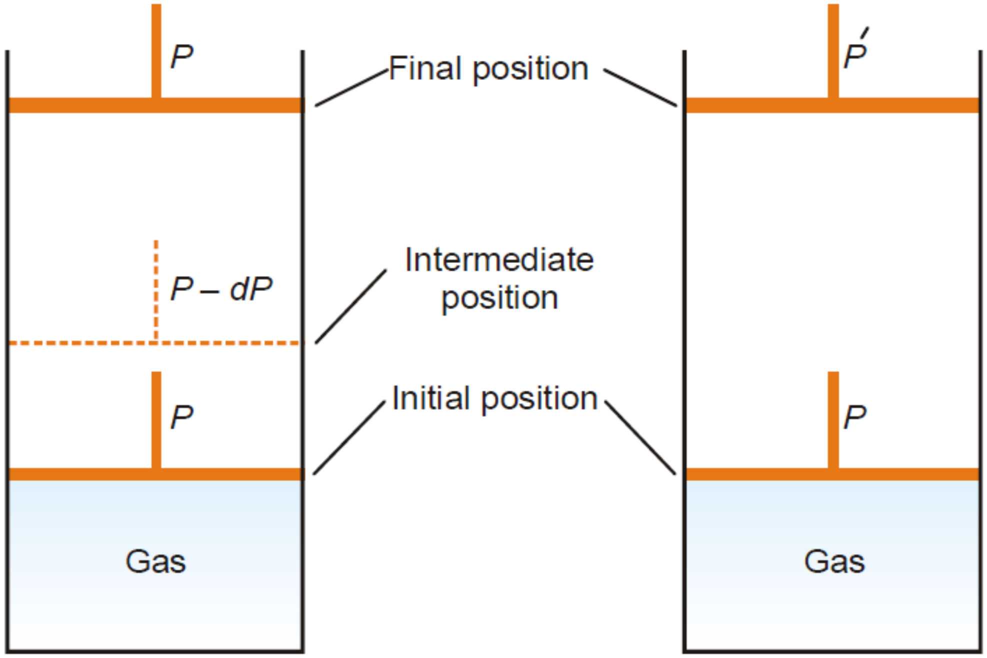
Adiabatic process: This occurs under the condition that heat can neither be added to not removed from the system. For an adiabatic process $dq = 0$

Cyclic Process: Cyclic process: It is a process in which a system undergoes a series of changes and ultimately comes back to the initial state. For a cyclic process $dE = 0$, $dH = 0$.

Thermodynamic Process

Reversible Process: A thermodynamic reversible process is one that takes place infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of the system.

Irreversible Process: When a process goes from the initial to the final state in a single step and cannot be carried in the reverse order, it is said to be an irreversible process.



Reversible Irreversible

Differences Between Reversible and Irreversible Processes

Reversible	Irreversible
1. It takes place in **infinite number** of infinitesimally small steps and it would take **infinite time** to occur.	**1.** It takes place in **finite time**.
2. It is **imaginary** as it assumes the presence of frictionless and weightless piston.	**2.** It is **real** and can be performed actually.
3. It is in **equilibrium state at all** stages of the operation.	**3.** It is in equilibrium state **only at the initial and final stages** of the operation.
4. **All changes are reversed** when the process is carried out in reversible direction.	**4.** After this type of process has occurred all changes do not return to the initial state by themselves.
5. It is extremely slow.	**5.** It proceeds at measureable speed.
6. Work done by a reversible process is greater than the corresponding irreversible process.	**6.** Work done by a irreversible process is smaller than the corresponding reversible process.

Sample Questions

1. Define the term ′Thermodynamics ′. Point out the scopes and limitations of thermodynamics.
2. What do you understand by thermodynamic system and surroundings? Explain open, closed and isolated systems.
3. Describe different types of thermodynamic processes.
4. Distinguish between isothermal and adiabatic processes.
5. Distinguish between reversible and irreversible processes.
6. Define and explain intensive and extensive thermodynamic properties?
7. What are state functions? How do they differ from path functions?

Lecture-4

Contents

- Work, heat and energy
- Sign convention of work and heat
- Molecular interpretation of work and heat
- Pressure-volume (*P*-*V*) work
- Reversible (*P*-*V*) work
- Irreversible (*P*-*V*) work
- Comparison between reversible and irreversible (*P*-*V*) work

Work, Heat and Energy

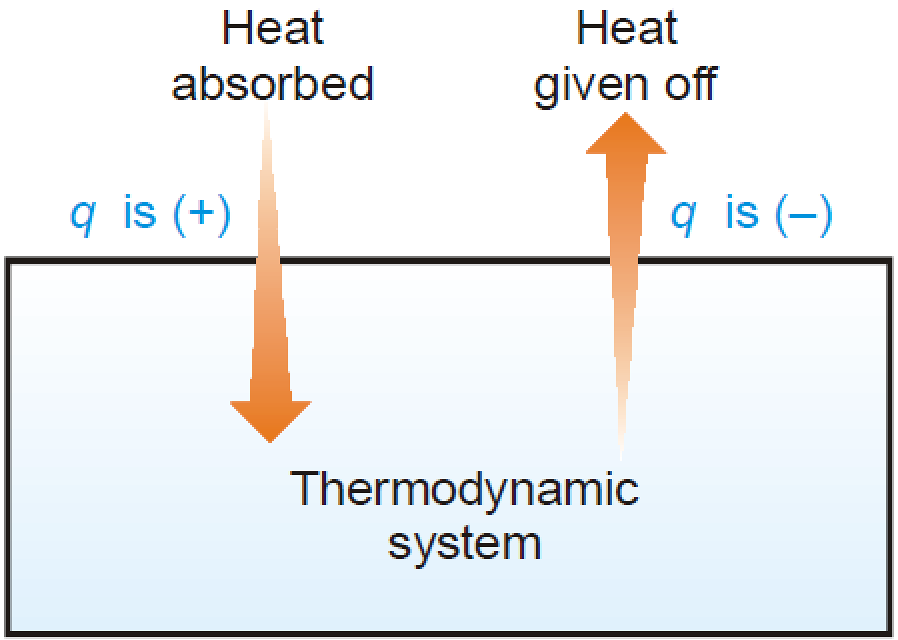
- Work is done to achieve motion against an opposing force.
- Energy is the capacity to do work.
- Heating is the transfer of energy that makes use of disorderly molecular motion.
- Work is the transfer of energy that makes use of organized motion.

Work, Heat and Energy

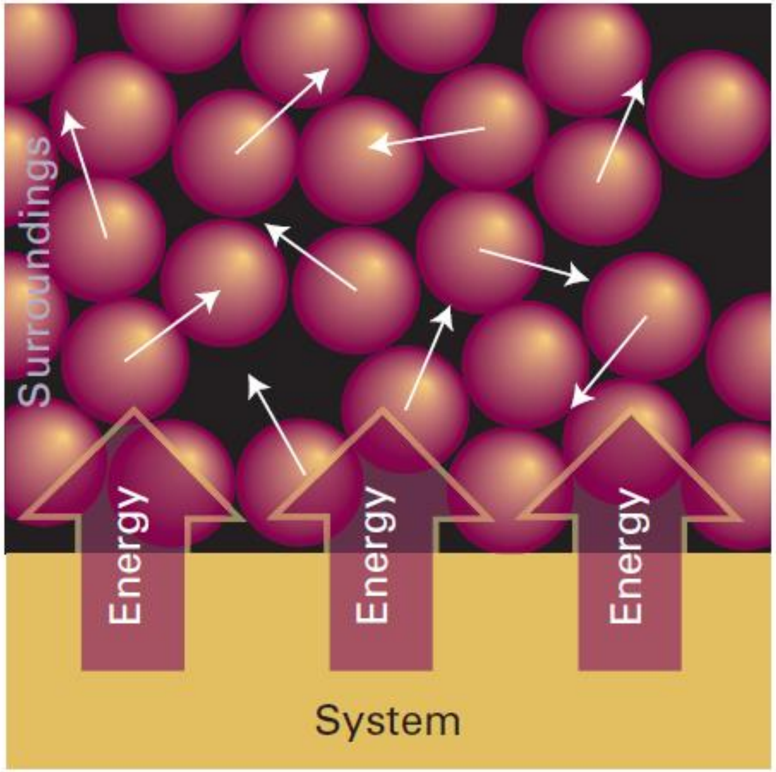
- Heat and work are defined only in terms of processes.
- Before and after the process of energy transfer between system and surroundings, heat and work do not exist.
- Heat is an energy transfer between system and surroundings due to a temperature difference.
- Work is an energy transfer between system and surroundings due to a macroscopic force acting through a distance.

Sign Convention of Heat and Work

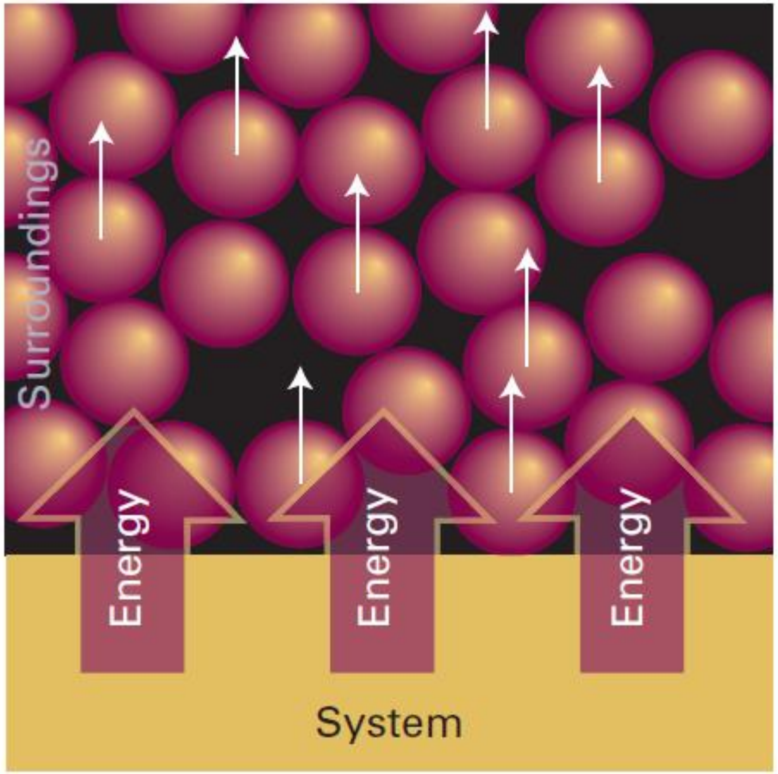
Heat flows into the system, *q* is positive (+)	Heat flows out of the system, *q* is negative (-)
Work is done on the system, *w* is positive (+)	Work is done by the system, *w* is negative (-)



The molecular interpretation of heat and work



When energy is transferred to the surroundings as **heat**, the transfer stimulates random motion of the atoms in the surroundings.



When a system does **work**, it stimulates orderly motion in the surroundings.

Ref: Atkins 9th edn, page 46

Pressure-Volume Work

In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as **pressure-volume work** or ***PV* work** or **expansion work.**

Consider a gas contained in a cylinder fitted with a frictionless piston. The pressure (force per unit area) of the gas, P, exerts a force on the piston. This can be balanced by applying an equal but opposite pressure from outside on the piston.

Let it be designated as P_{ext}. It is important to remember that it is the external pressure, P_{ext} and not the internal pressure of the gas itself which is used in evaluating work. This is true whether it be expansion or contraction.

Pressure-Volume Work

If the gas expands at constant pressure, the piston would move, say through a distance *l*.

Work = force × distance (by definition)

Or,

$$\boxed{w = f \times l \qquad \ldots(1)}$$

Since pressure is force per unit area,

$$\boxed{f = P_{\text{ext}} \times A \qquad \ldots(2)}$$

where *A* is the cross-section area of the piston.

From (1) and (2), we have

$$\begin{aligned} w &= P_{ext} \times A \times l \\ &= P_{ext} \times \Delta V \end{aligned}$$

where ΔV is the increase in volume of the gas.

$$\boxed{w = P_{ext} \times \Delta V}$$

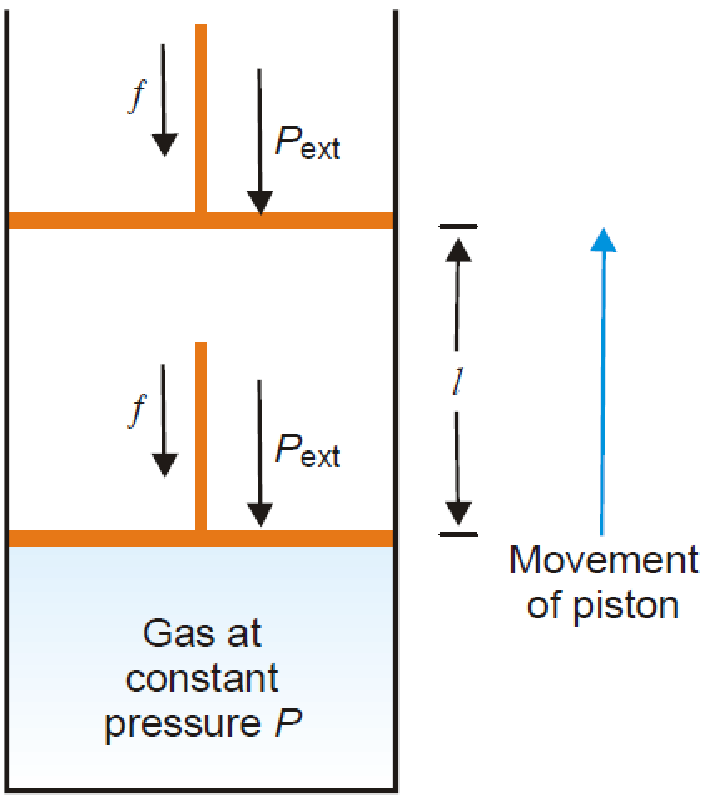
Pressure-Volume Work

Since the system (gas) is doing work on the surroundings (piston), it bears negative sign. Thus,

$$w = -P_{ext} \times \Delta V$$

The work done in compression of a gas can also be calculated. In that case the piston will move down and sign of the work will be positive.

$$w = P_{ext} \times \Delta V$$

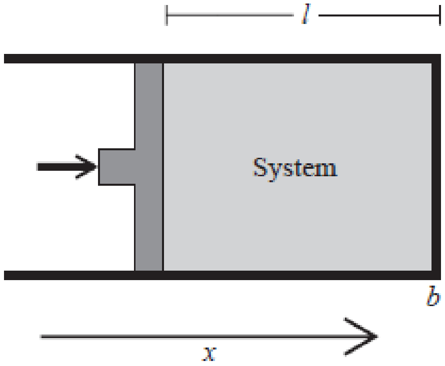


Reversible Pressure-Volume Work

- A **reversible process** is one where the system is always infinitesimally close to equilibrium.
- An infinitesimal change in conditions can reverse the process to restore both system and surroundings to their initial states.

Work done in a reversible process

$$dw_{\text{rev}} = -P\,dV$$

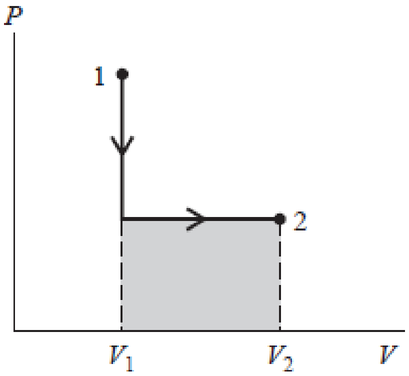


The total work *w* done:

$$w_{\text{rev}} = -\int_1^2 P\,dV$$

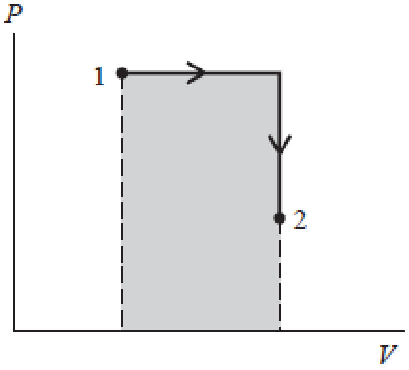
where 1 and 2 are the initial and final states of the system, respectively.

Reversible Pressure-Volume Work



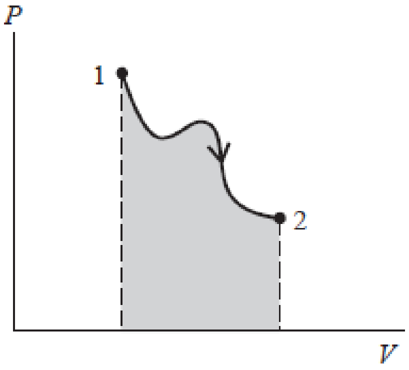
(a)

The pressure was reduced from P_1 to P_2 at constant volume V_1 by cooling the gas. Then the gas was expanded from V_1 to V_2 at constant pressure constant P_2 by heating.



(b)

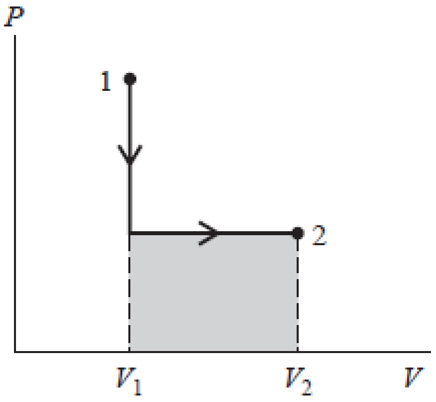
The gas was expanded from V_1 to V_2 at constant pressure constant P_2 by heating. Then the pressure was reduced from P_1 to P_2 at constant volume V_1 by cooling the gas.



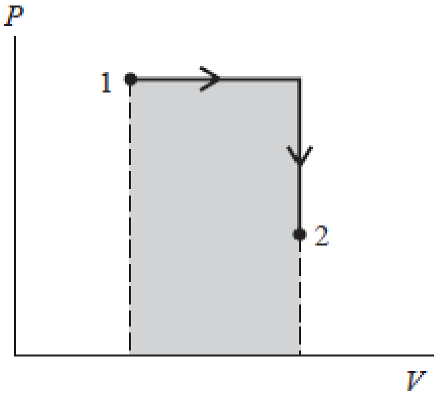
(c)

The independent variables V and T vary in an irregular way, as does the dependent variable P.

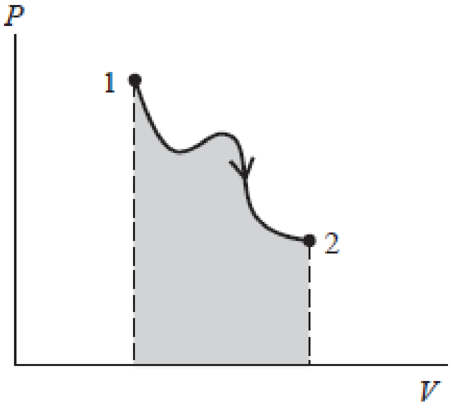
Reversible Pressure-Volume Work



(*a*)



(*b*)



(*c*)

Exercise

Find the work w_{rev} for processes (*a*) and (*b*) of if $P_1 = 3.00$ atm, $V_1 = 500\ \text{cm}^3$, $P_2 = 1.00$ atm, and $V_2 = 2000\ \text{cm}^3$. Also, find w_{rev} for the reverse of process (*a*). [Gas constant R = 8.314 J/(mol K) and R = 82.06 cm^3 atm/(mol K)]

For process (*a*)

$$w_{\mathrm{rev}} = -\int_1^2 P\,dV = -\int_{V_1}^{V_2} P_2\,dV = -P_2\int_{V_1}^{V_2} dV = -P_2V\Big|_{V_1}^{V_2}$$

$$= -P_2(V_2 - V_1) = -(1.00\ \mathrm{atm})(1500\ \mathrm{cm}^3)$$

$$= -1500\ \mathrm{cm}^3\ \mathrm{atm}\ \frac{8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}}{82.06\ \mathrm{cm^3\ atm\ mol^{-1}\ K^{-1}}} = -152\ \mathrm{J}$$

For reverse process (*a*)

$w_{\mathrm{rev}} = +152$ J

For process (*b*)

Hints: Use P_1 instead of P_2

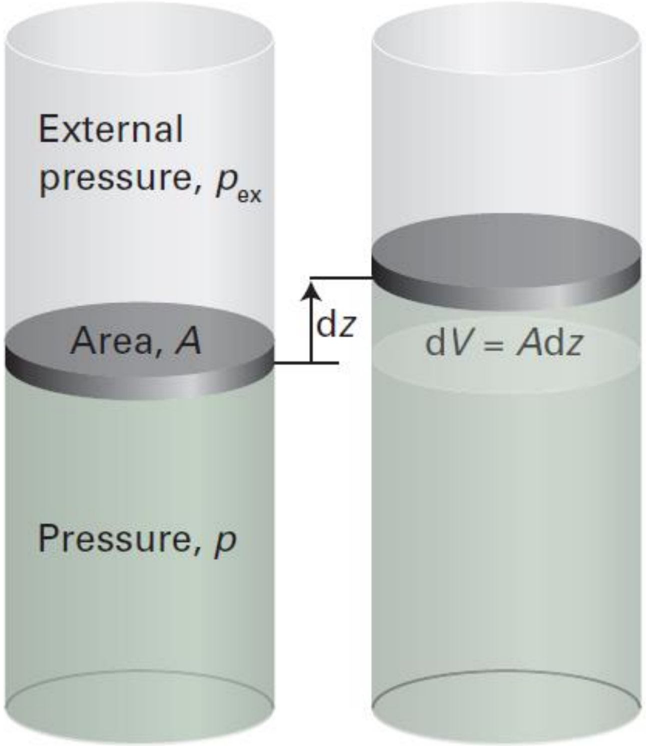
$w_{\mathrm{rev}} = -456$ J

Expansion work

The work done when the system expands by dV against a pressure p_{ex} is

$$dw = -p_{ex}dV$$

Expansion work



When a piston of area ***A*** moves out through a distance dz, it sweeps out a volume dV = Adz. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex}A$.

Expansion work

To obtain the total work done when the volume changes from an initial value V_i to a final value V_f we integrate this expression between the initial and final volumes:

$$w = -\int_{V_i}^{V_f} p_{ex} \mathrm{d}V$$

Free expansion

Free expansion is expansion against zero opposing force. It occurs when $p_{ex} = 0$.

Accordingly, $\mathrm{d}w = 0$ for each stage of the expansion.
Hence, overall:

$$w = 0$$

No work is done when a system expands freely. Expansion of this kind occurs when a gas expands into a vacuum.

Expansion work

Isothermal reversible expansion

Consider the isothermal, reversible expansion of a perfect gas.

The equation of state is $pV = nRT$.

At each stage $p = nRT/V$.
where, V = volume at that stage of the expansion.

The work of reversible isothermal expansion of a perfect gas from V_1 to V_2 at a temperature T is

$$w = -\int_{v_1}^{v_2} \frac{nRT}{V}\, dV$$

$$= -nRT \int_{v_1}^{v_2} \frac{dV}{V}$$

which integrates to give

$$w = -nRT \ln \frac{V_2}{v_1}$$

Since

$$P_1V_1 = P_2V_2$$

$$V_2/V_1 = P_1/P_2$$

$$w = -\,nRT\ \mathrm{In}\ \frac{P_1}{P_2} = -2.303\ nRT\ \log\ \frac{P_1}{P_2}$$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with the sign changed. Here the pressure on the piston, P_{ext}, is increased by dP which reduces the volume of the gas.

Expansion work

Problem

Calculate the work done when 50 g of iron reacts with hydrochloric acid to produce $FeC1_2$(aq) and hydrogen in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C.

(a) the volume cannot change, so no expansion work is done and $w = 0$

(b)

$$\Delta V = V_f - V_i \approx V_f = nRT/p_{ex}$$

$$w = -p_{ex}\Delta V \approx -p_{ex} \times \frac{nRT}{p_{ex}} = -nRT$$

$$w \approx -\frac{50\ \text{g}}{55.85\ \text{g mol}^{-1}} \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})$$

$$\approx -2.2\ \text{kJ}$$

Irreversible *P-V* Work

- Suppose we have an ideal gas contained in a cylinder with a piston. This time the process of expansion of the gas is performed irreversibly *i.e.*, by instantaneously dropping the external pressure, P_{ex}, to the final pressure P_2.
- The work done by the system is now against the pressure P_2 throughout the whole expansion and is given by the following expression :

$$w_{irr} = -Pex \int_{v_1}^{v_2} dV$$

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

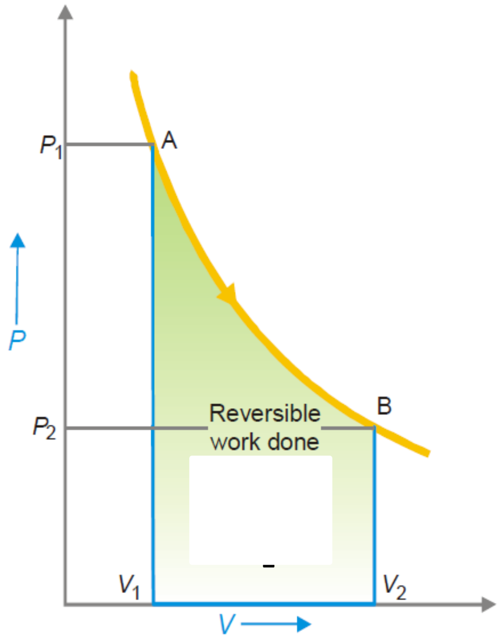
$$= -P_2 \Delta V$$

Comparison of work done in reversible and irreversible processes

Work done in reversible expansion,

$$w_{rev} = -\int_{V_1}^{V_2} P dV$$

which is represented by the shaded area in figure (*a*).

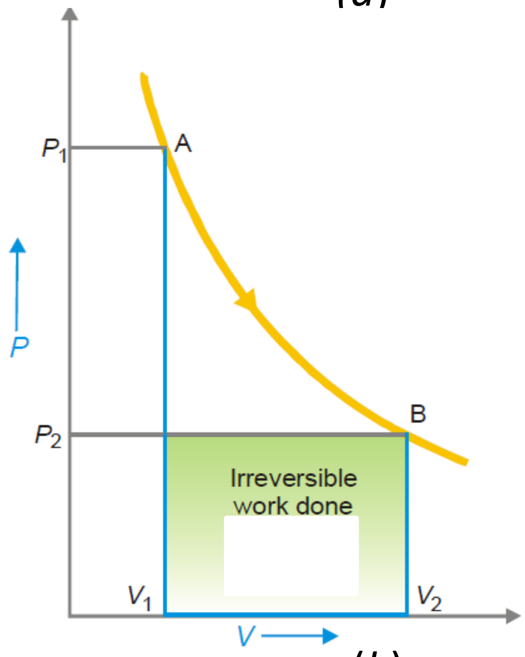


(*a*)

Work done in irreversible expansion,

$$w_{irrev} = -P_2(V_2 - V_1)$$

which is shown by the shaded area in figure (*b*).



(*b*)

Mechanical work is not a state function

In both the processes, the state of the system has changed from *A* to *B* but the work done is less in the irreversible expansion than in the reversible expansion. **Thus mechanical work is not a state function as it depends on the path by which the process is performed rather than on the initial and final states. It is a path function.**

Maximum work is done in the reversible expansion of a gas

The work always depends on the external pressure, *P*ext. The larger the P_{ext} the more work is done by the gas. But the P_{ext} on the gas cannot be more than the pressure of the gas, P_{gas} or a compression will take place. Thus the largest value P_{ext} can have without a compression taking place is equal to P_{gas}. But an expansion that occurs under these conditions is the reversible expansion.
Thus, maximum work is done in the reversible expansion of a gas.

Lecture-5

Contents

- Internal Energy
- Zeroth law of thermodynamics
- First law of thermodynamics
- Enthalpy
- Exercise

The Total Energy

In addition to macroscopic kinetic energy K and potential energy V, a body possess its internal energy U.

Therefore, The total energy E of a body is

$$\boxed{E = K + V + U}$$

where, $K = \frac{1}{2}mV^2$ and $V = mgh$

The internal energy

Internal energy, U consists of: molecular translational, rotational, vibrational, and electronic energies; the relativistic rest-mass energy $m_{\text{rest}}c^2$ of the electrons and the nuclei; and potential energy of interaction between the molecules.

Change in internal Energy, $\Delta U = U_f - U_i$

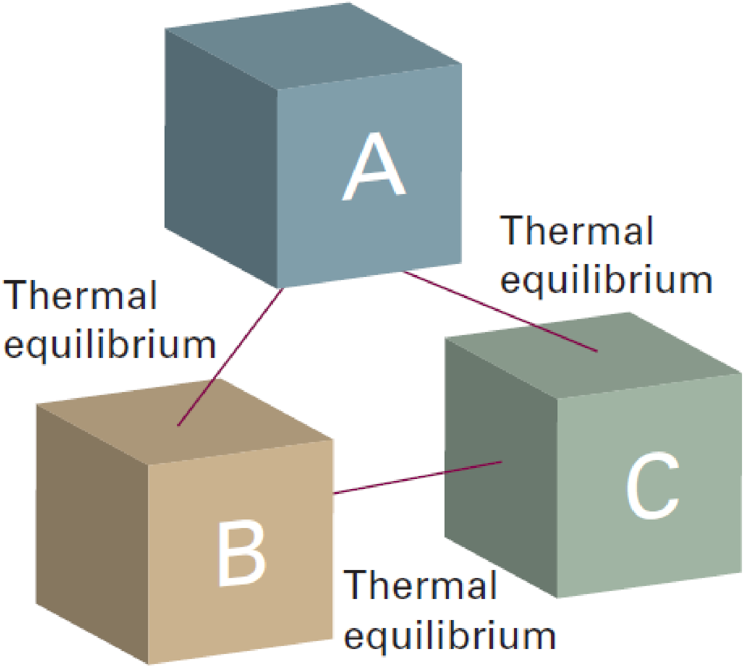
when a system changes from an initial state i with internal energy U_i to a final state *f* of internal energy U_f

The internal energy

- Internal energy is a state function.
- Its value depends only on the current state of the system.
- The internal energy is an extensive property of a system and is measured in joules (1 J = 1 kg m^2 s^{-2})
- The molar internal energy, $U_m = U/n$ is an intensive property and commonly reported kJ mol^{-1}.

Zeroth Law of Thermodynamics

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.

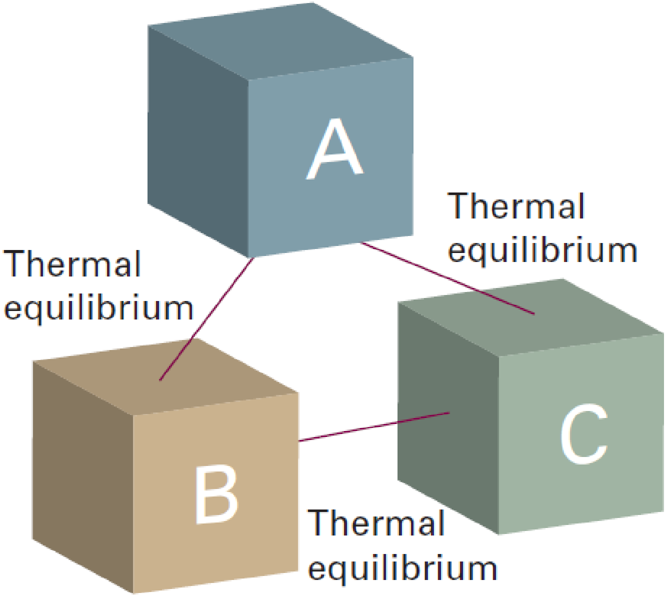


Zeroth Law of Thermodynamics

The Zeroth Law justifies the concept of temperature and the use of a **thermometer.**

Suppose that B is a glass capillary containing liquid mercury. Then, when A is in contact with B, the mercury column has a certain length.

According to the Zeroth Law, if the mercury column in B has the same length when it is placed in thermal contact with another object C, then we can predict that no change of state of A and C will occur when they are in thermal contact.



First Law of Thermodynamics

The first law may be stated in different forms:

(1) Energy can neither be created nor destroyed; it can only be converted from one form to another.

(2) The total energy of an isolated system is constant.

(3) It is impossible to construct a perpetual motion machine which will create energy out of nothing.

(4) If work is produced during a cyclic process, an equivalent amount of heat must also be consumed.

Mathematical Formulation of the First Law

When heat is applied to a system, the internal energy of the system will increase if no work is done ($\Delta U = q$).

Similarly, if work is done on the system in absence of heat the internal energy will be increased ($\Delta U = w$).

If heat and work processes occur simultaneously, the net change in internal energy of a system is equal to sum of the heat applied (q) and work done (w). Mathematically, we can represent this as

$$\Delta U = q + w \qquad \ldots\ldots\ldots\ldots..(1)$$

For infinitesimal change eqn. (1) may be written as

$$dU = dq + dw$$

A brief illustration

If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then the change in the internal energy of the motor each second is

$$\Delta U = -2\text{ kJ} - 15\text{ kJ} = -17\text{ kJ}$$

Suppose that, when a spring was wound, 100 J of work was done on it but 15 J escaped to the surroundings as heat. The change in internal energy of the spring is

$$\Delta U = 100\text{ J} - 15\text{ J} = +85\text{ J}$$

A note on good practice

Always include the sign of ΔU (and of ΔX in general), even if it is positive.

Enthalpy

The change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume.

$\mathrm{d}U \neq \mathrm{d}q$

At constant *p*

Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work.

$\mathrm{d}U < \mathrm{d}q$

In case of expansion

In this case the energy supplied as heat at constant pressure is equal to the change in another thermodynamic property of the system, the enthalpy, *H*.

$\mathrm{d}H = \mathrm{d}q$

At constant *p*

Enthalpy

The **enthalpy** *H* of a thermodynamic system whose internal energy, pressure, and volume are *U*, *P*, and *V* is defined as

$$\boxed{H \equiv U + PV}$$

Since *U*, *P*, and *V* are state functions, *H* is a state function.

The motivation for giving a special name to the state function $U + PV$ is that this combination of *U*, *P*, and *V* occurs often in thermodynamics.

$\Delta H = q_P$

Let q_P be the heat absorbed in a constant-pressure process in a closed system. The first law $\Delta U = q + w$ gives

$$U_2 - U_1 = q + w = q - \int_{V_1}^{V_2} P\,dV$$

$$= q_P - P\int_{V_1}^{V_2} dV = q_P - P(V_2 - V_1)$$

$$q_P = U_2 + PV_2 - U_1 - PV_1$$

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1) = H_2 - H_1$$

$$\boxed{\Delta H = q_P \qquad \text{const. } P\text{, closed syst., } P\text{-}V \text{ work only}}$$

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

For any change of state, the enthalpy change is

$$\Delta H = H_2 - H_1$$

$$= U_2 + P_2V_2 - (U_1 + P_1V_1) = \Delta U + \Delta(PV)$$

where $\Delta(PV) \equiv (PV)_2 - (PV)_1 = P_2V_2 - P_1V_1$.

For a constant-pressure process,

$$P_2 = P_1 = P$$

and $\Delta(PV) = PV_2 - PV_1 = P\,\Delta V$.

Therefore

$$\boxed{\Delta H = \Delta U + P\,\Delta V \qquad \text{const. } P}$$

$\Delta U = q_V$

Since U and V are extensive, H is extensive. The molar enthalpy of a pure substance is

$$H_m = H/n = (U + PV)/n = U_m + PV_m.$$

Consider now a constant-volume process. If the closed system can do only P-V work, then w must be zero, since no P-V work is done in a constant-volume process.

The first law $\Delta U = q + w$ then becomes for a constant-volume process

$\Delta U = q_V$ closed syst., P-V work only, V const.

Now, $\Delta H = q_P$ closed syst., P-V work only, P constant

In a constant-pressure process H plays a role analogous to that played by U in a constant-volume process.

For Condensed phases

- Now we have $\Delta H = \Delta U + \Delta(PV)$.

- Because solids and liquids have comparatively small volumes and undergo only small changes in volume, in nearly all processes that involve only solids or liquids (*condensed* phases) at low or moderate pressures, the $\Delta(PV)$ term is negligible compared with the ΔU term.

- For condensed phases not at high pressures, the enthalpy change in a process is essentially the same as the internal-energy change: $\Delta H \approx \Delta U$.

- H depends only on T for a perfect gas, for isothermal expansion, $\Delta H = 0$.

Exercises

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermodynamic data are for 298.15 K.

1. A chemical reaction takes place in a container of cross-sectional area 100 cm^2. As a result of the reaction, a piston is pushed out through 10 cm against an external pressure of 1.0 atm. Calculate the work done by the system.
2. A chemical reaction takes place in a container of cross-sectional area 50.0 cm^2. As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 121 kPa. Calculate the work done by the system.
3. A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 dm^3 to 44.8 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU, and ΔH.
4. A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 dm^3 to 31.7 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU, and ΔH.

Important relations

R = 8.314 J K^{-1} mol^{-1} = 82.06 cm^3 atm mol^{-1} K^{-1}

- **Pressure**

1 atm = 101.325 kPa

1 Pa = 1 kg m^{-1} s^{-2} = 1 N m^{-2}

1 bar = 10^5 Pa

- **Force**

1 N = 1 kg m s^{-2}

- **Energy**

Joule, J = 1 kg m^2 s^{-2} = 1 N m = 1 Pa m^3

Hints for solving the problems

1. $w = -P_{\text{ext}} \times \Delta V$

2. $w = -P_{\text{ext}} \times \Delta V$

3. (a) For isothermal expansion, $\Delta U = \Delta H = 0$

Work done in an isothermal reversible expansion,

$$w = -nRT \ln \frac{V_2}{V_1}$$

$$q = -w$$

(b) For isothermal expansion, $\Delta U = \Delta H = 0$

Expansion work against constant pressure,

$$w = -P_{\text{ext}} \times \Delta V$$

$$q = -w$$

(c) For isothermal expansion, $\Delta U = \Delta H = 0$

Expansion work against zero pressure,

$$w = -P_{\text{ext}} \times \Delta V = 0$$

$$q = -w = 0$$

Lecture-6

Contents

- Relation between H and U
- Heat Capacities
- Heat capacity at constant volume, C_v
- Heat capacity at constant pressure, C_p
- Relation between C_p and C_v

Relation between *H* and *U*

For an ideal gas

$$H = U + pV = U + nRT$$

Change in enthalpy under isothermal conditions is

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

Change in enthalpy under constant pressure conditions is

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

Exercise

- Calculate the value of $\Delta H - \Delta U$ for the following reaction at 298 K temperature: $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$. [Answer: $\approx$ -7.4 kJ]
- Calculate the value of $\Delta H - \Delta U$ for the following reaction at 298 K temperature: $N_2(g) + 3H_2(g) \rightarrow 2\,NH_3(g)$. [Answer: -5.0 kJ]
- Calculate the difference between ΔH and ΔU when 1.0 mol Sn(s, grey) of density 5.75 g cm^{-3} changes to Sn(s, white) of density 7.31 g cm^{-3} at 10.0 bar. [Answer: $\Delta H - \Delta U$ = -4.4 J]

Hints: $\Delta H_m - \Delta Um = pM\left(\frac{1}{\rho(w)} - \frac{1}{\rho(g)}\right)$

Heat Capacities

Heat capacity is defined as the amount of heat required to rise the temperature of a substance through 1 degree.

$$\text{Heat capacity, } C = \frac{dq}{dT}$$

- For one gram of a substance it is known as specific heat.
- For the one mole it is molar heat capacity ($C_m = {}^{C}/_{n}$).

Heat capacity at constant volume, C_v

Heat capacity at constant volume,

$$C_v = dq_v / dT$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \qquad \text{[since } dU = dq_v\text{]}$$

$$dU = dq_v = C_v dT$$

- For finite change, we have

$$\Delta U = q_v = \int_{T_1}^{T_2} C_v dT$$

- If C_v is considered to be independent of temperature in the range T_1 to T_2, then

$$\Delta U = q_v = C_v \Delta T$$

Heat capacity at constant pressure, C_p

Heat capacity at constant pressure

$$C_p = {}^{dq_p}\!/_{dT} = \left(\frac{\partial H}{\partial T}\right)_p$$

- For finite change, we have

$$\Delta H = q_p = \int_{T_1}^{T_2} C_p\, dT$$

- If C_p is considered to be independent of temperature in the range T_1 to T_2, then

$$\Delta H = q_p = C_p \Delta T$$

Relation between C_p and C_v

This can be shown from thermodynamic point of view.

$C_p = \left(\frac{\partial H}{\partial T}\right)_p$ and $H = U + PV$

From these two equations we get,

$$C_p = \left[\frac{\partial (U+PV)}{\partial T}\right]_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \qquad (1)$$

The internal energy U can be written as a function to two variables T and V,

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

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

Dividing both sides by dT and imposing constant pressure condition, it follows that

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

$$= C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \qquad (2)$$

Substituting equation (2) into equation (1) and rearranging we get

$$C_p = C_v + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p \qquad (3)$$

Equation (3) is one form of relationship between C_p and C_v.

For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$

So that $$C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_p \qquad (4)$$

- The state function $(\partial U/\partial V)_T$ has dimensions of pressure and is sometimes called the *internal pressure* and denoted as π_T.

For an ideal gas $PV = nRT$. Differentiating both sides of this equation of state with respect to temperature and imposing the condition of constant pressure one can obtain,

$$P\left(\frac{\partial V}{\partial T}\right)_p = \frac{\partial (nRT)}{\partial T} = nR \qquad (5)$$

Combining equations (4) & (5) we obtain

$$C_p - C_v = nR \qquad (6)$$

Therefore, $C_p > C_v$, because R is positive.

For molar heat capacities, $n = 1$

$$\boxed{C_{p,m} - C_{v,m} = R}$$

Lecture-7

Contents

Mathematical background

- Derivatives
- Partial derivatives
- Three useful partial-derivative identities
- Total differentials

Derivatives

Let a and n be constants, and let u and v be functions of x; $u \quad u(x)$ and $v = v(x)$. Then, one finds the following derivatives:

$$\frac{da}{dx} = 0$$

$$\frac{d(au)}{dx} = a\frac{du}{dx}$$

$$\frac{dx^n}{dx} = nx^{n-1}$$

$$\frac{de^{ax}}{dx} = ae^{ax}$$

$$\frac{d \ln ax}{dx} = \frac{1}{x}$$

$$\frac{d \sin ax}{dx} = a \cos ax$$

$$\frac{d \cos ax}{dx} = -a \sin ax$$

$$\frac{d(u+v)}{dx} = \frac{du}{dx} + \frac{dv}{dx}$$

$$\frac{d(uv)}{dx} = v\frac{du}{dx} + u\frac{dv}{dx}$$

$$\frac{d(u/v)}{dx} = \frac{1}{v}\frac{du}{dx} - \frac{u}{v^2}\frac{dv}{dx}$$

Partial Derivatives

- A **partial derivative** of a function of more than one variable, such as *f*(*x*,*y*), is the slope of the function with respect to one of the variables, all the other variables being held constant.
- It may be used to determine how the function changes when more than one variable changes by an infinitesimal amount. Thus, if *f* is a function of *x* and *y*, then when *x* and *y* change by *dx* and *dy*, respectively, *f* changes by

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

How are partial derivatives found?

To find $(\partial z/\partial x)_y$ we take the ordinary derivative of z with respect to x while regarding y as a constant.

For example, if $z = x^2y^3 + e^{yx}$, then

- $(\partial z/ \partial x)_y = 2xy^3 + ye^{yx}$; and
- $(\partial z/ \partial y)_x = 3x^2y^2 + xe^{yx}$

Exact differentials

Successive partial derivatives may be taken in any order

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$$

This equation is the basis of a test of an exact differential.

Brief illustration

Suppose that $f(x,y) = ax^3y + by^2$

Hence, $df = 3ax^2y\,dx + (ax^3+2by)\,dy$

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = 3ax^2 \qquad \text{and} \qquad \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = 3ax^2$$

Thus, *df* is an exact differential.

Now, suppose that $df = 3ax^2y\,dx + (ax^2+2by)\,dy$

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = 3ax^2 \qquad \text{and} \qquad \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = 2ax$$

Thus, *df* is not an exact differential.

Total Differential

Let $z = f(x, y)$. If now both x and y undergo infinitesimal changes, the infinitesimal change in z is the sum of the infinitesimal changes due to dx and dy:

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

In this equation, dz is called the **total differential** of $z(x, y)$.

The total differential of a function of more than two variables. For example, if $z = z(r, s, t)$, then

$$dz = \left(\frac{\partial z}{\partial r}\right)_{s,t} dr + \left(\frac{\partial z}{\partial s}\right)_{r,t} ds + \left(\frac{\partial z}{\partial t}\right)_{r,s} dt$$

Three useful partial-derivative identities can be derived from the total differential,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad \text{--- (1)}$$

- For an infinitesimal process in which *y* does not change, the infinitesimal change *dy* is 0, and

$$dz_y = \left(\frac{\partial z}{\partial x}\right)_y dx_y \qquad \text{------------ (2)}$$

where the *y* subscripts on *dz* and *dx* indicate that these infinitesimal changes occur at constant *y*.

Division by dz_y gives

$$1 = \left(\frac{\partial z}{\partial x}\right)_y \frac{dx_y}{dz_y} = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y$$

and $$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{(\partial x/\partial z)_y} \qquad \text{------------ (3)}$$

- For an infinitesimal process in which *z* stays constant

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx_z + \left(\frac{\partial z}{\partial y}\right)_x dy_z$$

Dividing by dy_z *and recognizing that* dx_z/dy_z *equals* $(\partial x/\partial y)_z$, *we get*

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x$$

and $$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x = -\frac{1}{(\partial y/\partial z)_x}$$

then $$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad \text{-----}\ (4)$$

- Finally, let *dy* in (1) be zero so that (2) holds. Let *u* be some other variable. Division of (2) by du_y gives

$$\frac{dz_y}{du_y} = \left(\frac{\partial z}{\partial x}\right)_y \frac{dx_y}{du_y}$$

$$\left(\frac{\partial z}{\partial u}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_y \qquad \text{----- (5)}$$

Lecture-8

Contents

- Change in internal energy
- Changes in internal energy at constant pressure
- Expansion coefficient, α
- Isothermal Compressibility, κ_T
- Change in enthalpy with temperature and pressure
- Joule experiment

Change in internal energy

Because the internal energy is a function of the volume and the temperature, when these two quantities change, the internal energy changes by

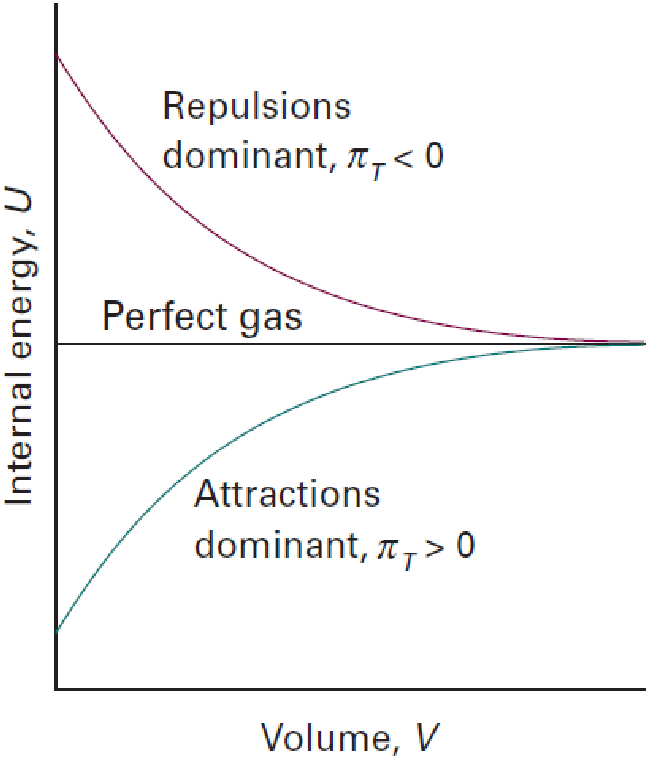
$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

or, $dU = \pi_T dV + C_V dT$ ----------(1)

where, $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$ = internal pressure

Illustrations of internal pressure, $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$

- When there are no interactions between the molecules, *U* is independent of their separation. Therefore, for a perfect gas we can write $\pi_T = 0$.
- If the attractive forces between the particles dominate the repulsive forces, then $dU > 0$ as $dV > 0$. In this case $\pi_T > 0$.
- When repulsions dominant, $\pi_T < 0$.



Changes in internal energy at constant pressure

Partial derivatives have many useful properties. Skilful use of them can often turn some unfamiliar quantity into a quantity that can be recognized, interpreted, or measured.

As an example, to find how the internal energy varies with temperature when the pressure rather than the volume of the system is kept constant.

Dividing both sides of eqn (1) by d*T* and imposing constant pressure condition one get

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V \qquad \text{----------(2)}$$

For a perfect gas, $\pi_T = 0$, and hence,

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V \qquad \text{----------(3)}$$

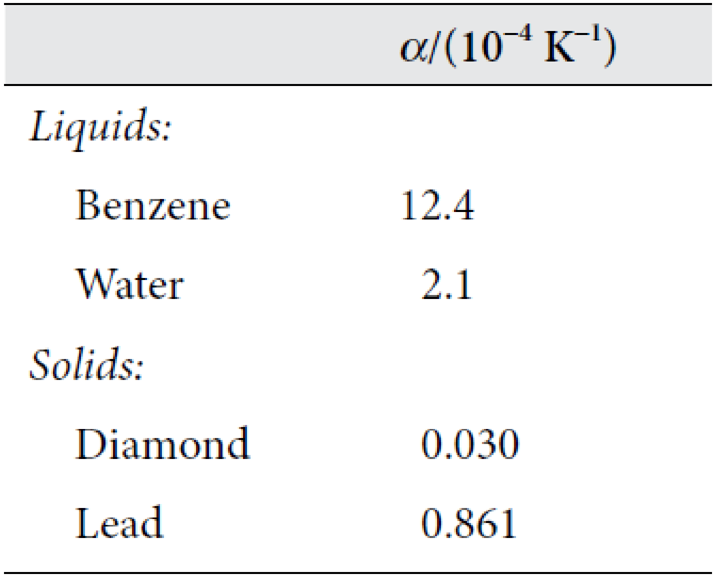
Expansion coefficient, α

Eqn (2) can be written as

$$\left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V \qquad \text{----------(4)}$$

where, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ = expansion coefficient

Note that, α is a recognizable quantity. A large value of α means that the volume of the sample responds strongly to changes in temperature.



	$\alpha/(10^{-4}\ \mathrm{K}^{-1})$
Liquids:	
Benzene	12.4
Water	2.1
Solids:	
Diamond	0.030
Lead	0.861

Derive an expression for the expansion coefficient of a perfect gas and give physical interpretation of the result.

The solution

Because $pV = nRT$, write

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{\partial (nRT/p)}{\partial T}\right)_p$$

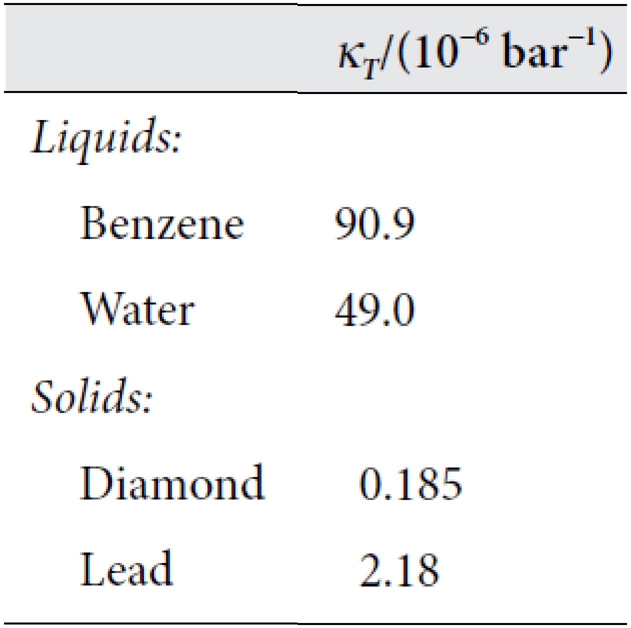
$$= \frac{1}{V} \times \frac{nR}{p} = \frac{nR}{nRT} = \frac{1}{T}$$

The physical interpretation of this result is that the higher the temperature, the less responsive is the volume of a perfect gas to a change in temperature.

Isothermal Compressibility, κ_T

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

- The isothermal compressibility is a measure of the fractional change in volume when the pressure is increased;
- The negative sign in the definition ensures that the compressibility is a positive quantity, because an increase of pressure, implying a positive dp, brings about a reduction of volume, a negative dV.



	$\kappa_T/(10^{-6}\ \mathrm{bar}^{-1})$
Liquids:	
Benzene	90.9
Water	49.0
Solids:	
Diamond	0.185
Lead	2.18

Derive an expression for the Isothermal Compressibility, κ_T of a perfect gas.

The solution

Because $pV = nRT$, write

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(\frac{\partial (nRT/p)}{\partial p}\right)_T$$

$$= \frac{1}{V} \times \frac{nRT}{p^2} = \frac{nRT}{nRT.p} = \frac{1}{p}$$

The physical interpretation of this result is that the higher the pressure, the less responsive is the volume of a perfect gas to a change in pressure.

Change in enthalpy with temperature and pressure

Deriving an expression for the variation of enthalpy with pressure and temperature

Consider a closed system of constant composition. Because *H* is a function of *p* and *T*, when these two quantities change by an infinitesimal amount, the enthalpy changes by

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T$$

The second partial derivative is C_p. The task at hand is to express $(\partial H/\partial p)_T$ in terms of recognizable quantities. If the enthalpy is constant, then $\mathrm{d}H = 0$ and

$$\left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p = -C_p \mathrm{d}T \quad \text{at constant } H$$

Division of both sides by *dp* then gives

$$\left(\frac{\partial H}{\partial p}\right)_T = -C_p\left(\frac{\partial T}{\partial p}\right)_H = -C_p\mu$$

where the **Joule–Thomson coefficient**, μ (mu), is defined as

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$

Joule–Thomson coefficient [definition]

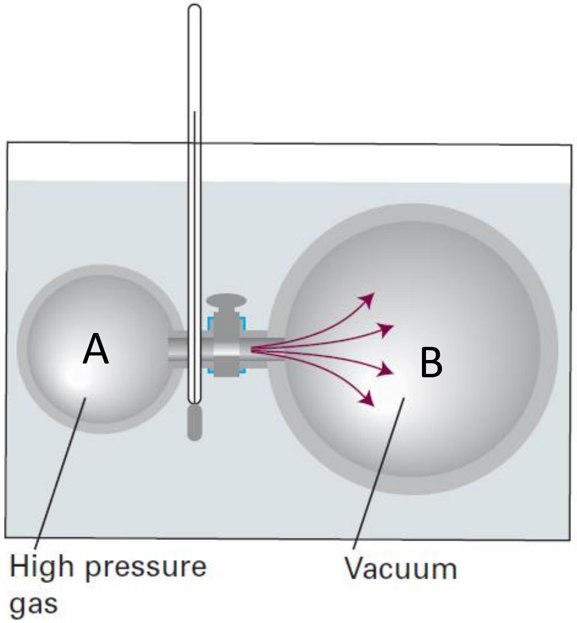
It follows that

$$\mathrm{d}H = -\mu C_p\mathrm{d}p + C_p\mathrm{d}T$$

Evaluation of $(\partial U/\partial V)_T$ for gases: The Joule Experiment

In 1843 Joule tried to determine $(\partial U/\partial V)_T$ for a gas by measuring the temperature change after free expansion of the gas into a vacuum. This experiment was repeated by Keyes and Sears in 1924 with an improved setup.

Initially, chamber A is filled with a gas, and chamber B is evacuated. The valve between the chambers is then opened. After equilibrium is reached, the temperature change in the system is measured by the thermometer.



From first law of thermodynamics,

$\Delta U = q + w$ for a closed system

Because the system is surrounded by adiabatic walls, $q = 0$.
For expansion into a vacuum, $w = 0$.

Hence, $\Delta U = 0 + 0 = 0$

This is a constant-energy process.

The experiment measures the temperature change with change in volume at constant internal energy, $(\partial T/ \partial V)_U$.

More precisely, the experiment measures $\Delta T/ \Delta V$ at constant U.

How is the measured quantity $(\partial T/\partial V)_U = \mu_J$ *(Joule coefficient)* related to $(\partial U/\partial V)_T = \pi_T$?

The variables in these two partial derivatives are the same (namely, *T, U,* and *V*).

Hence we can use, $(\partial x/\partial y)_z(\partial y/\partial z)_x(\partial z/\partial x)_y = -1$

$$\left(\frac{\partial T}{\partial U}\right)_V\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_U = -1$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left[\left(\frac{\partial T}{\partial U}\right)_V\right]^{-1}\left[\left(\frac{\partial V}{\partial T}\right)_U\right]^{-1} = -\left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_U$$

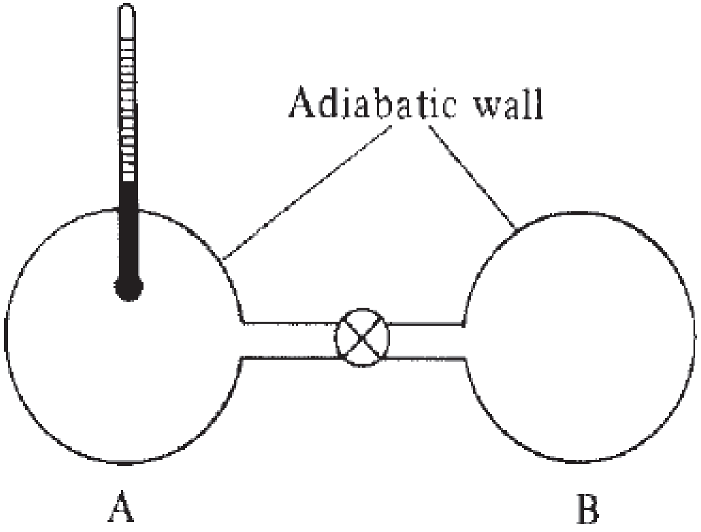
$$\left(\frac{\partial U}{\partial V}\right)_T = -C_V\mu_J$$

where $(\partial z/\partial x)_y = 1/(\partial x/\partial z)_y$, $(\partial U/\partial T)_V = C_V$, and $\mu_J = (\partial T/\partial V)_U$

Joule's experiment gave zero for μ_J and hence zero for $(\partial U/\partial V)_T$.

Criticism of Joule’s Experiment

- Joule’s experiment gave zero for μ_J and hence zero for $(\partial U/\partial V)_T$.
- However, his setup was so poor that his result was meaningless.
- The 1924 Keyes–Sears experiment showed that $(\partial U/\partial V)_T$ is small but definitely nonzero for gases.
- Because of experimental difficulties, only a few rough measurements were made.



Figure

The Keyes–Sears modification of the Joule experiment.

Lecture-9

Contents

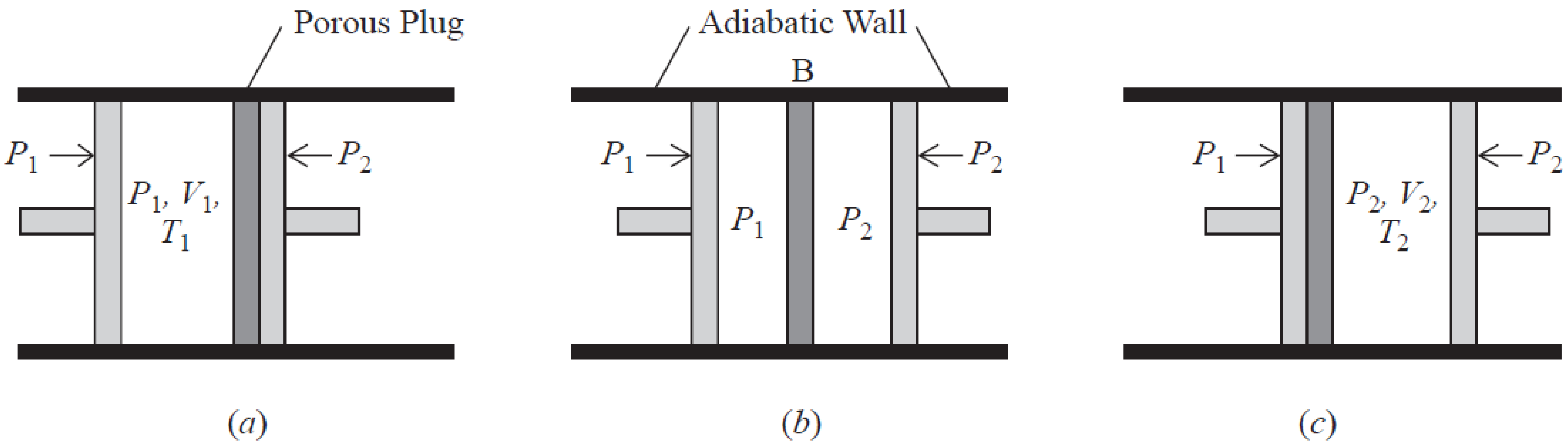
- Joule–Thomson experiment
- Construction of isenthalpic curve
- Analysis of isenthalpic curve
- Joule–Thomson throttling for gas liquefaction

The Joule-Thomson Effect

The cooling effect observed when a gas is adiabatically expanded from a high pressure region to a low pressure region through a throttle valve or porous plug is called Joule-Thomson effect.

The cooling effect in the Joule-Thomson experiment is attributed to the intermolecular attractions of the molecules. An expanding gas has to do work in order to overcome the attractive force among the molecules. The work is done at the cost of internal energy as the process is adiabatic. As a result the temperature of the expanding gas will fall.

Joule–Thomson experiment (1853)



The Joule–Thomson experiment involves the slow throttling of a gas through a rigid, porous plug. The system is enclosed in adiabatic walls. The left piston is held at a fixed pressure p_1. The right piston is held at a fixed pressure $p_2 < p_1$. The partition B is porous but not greatly so. This allows the gas to be slowly forced from one chamber to the other. Because the throttling process is slow, pressure equilibrium is maintained in each chamber. Essentially all the pressure drop from p_1 to p_2 occurs in the porous plug.

Calculation of *w*

- The exchange of work between system and surroundings occurs solely at the two pistons.
- Since pressure equilibrium is maintained at each piston, we can use $dw_{rev} = -p\,dV$ to calculate the work at each piston.
- The left piston does work w_L on the gas. We have $dw_L = -p_L dV = -p_1 dV$, where subscripts L and R are used for left and right.
- Let all the gas be throttled through. The initial and final volumes of the left chamber are V_1 and 0, so

$$w_L = -\int_{V_1}^{0} p_1 dV = -p_1 \int_{V_1}^{0} dV = -p_1(0 - V_1) = p_1 V_1$$

The right piston does work dw_R on the gas. (w_R is negative, since the gas in the right chamber does positive work on the piston.) We have

$$w_R = -\int_0^{V_2} p_2 dV = -p_2V_2$$

The work done on the gas is

$$w = wL + w_R = p_1V_1 - p_2V_2$$

The first law for this adiabatic process ($q = 0$) gives

$$U_2 - U_1 = q + w = w,$$

so $U_2 - U_1 = p_1V_1 - p_2V_2$

or $U_2 + p_2V_2 = U_1 + p_1V_1$.

Since $H = U + pV$, we have

$H_2 = H_1$ *or* $\Delta H = 0$

isenthalpic process

The initial and final enthalpies are equal in a Joule–Thomson expansion.

Measurement of the temperature change $T = T_2 - T_1$ in the Joule–Thomson experiment gives $\Delta T/\Delta p$ at constant H. This may be compared with the Joule experiment, which measures $\Delta T/\Delta V$ at constant U.

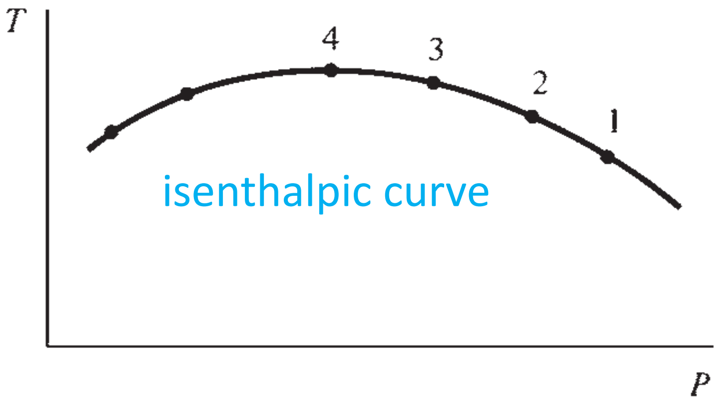
We define the Joule–Thomson coefficient μ by

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$

μ is the ratio of infinitesimal changes in two intensive properties and therefore is an intensive property. Like any intensive property, it is a function of T and p (and the nature of the gas).

Construction of isenthalpic curve

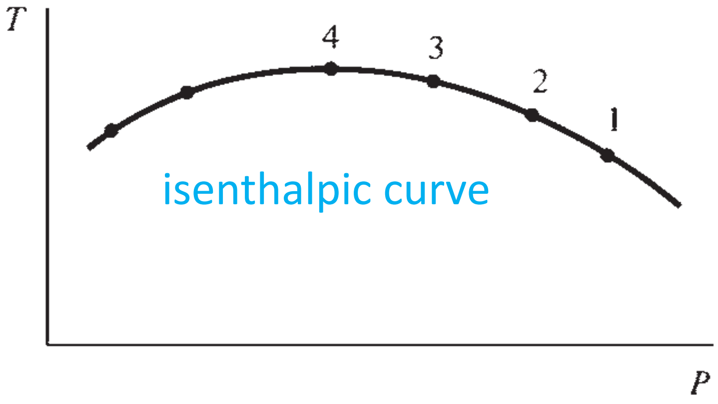
- A single Joule–Thomson experiment yields only $(\Delta T/\Delta p)_H$.
- To find $(\Delta T/\Delta p)_H$ values start with some initial p_1 and T_1, pick a value of p_2 less than p_1 and do the throttling experiment, measuring T_2.
- Then plot the two points (T_1, p_1) and (T_2, p_2) on a T-p diagram; these are points 1 and 2. Since $\Delta H = 0$ for a Joule–Thomson expansion, states 1 and 2 have equal enthalpies.
- A repetition of the experiment with the same initial p_1 and T_1 but with the pressure on the right piston set at a new value p_3 gives point 3 on the diagram.
- Several repetitions, each with a different final pressure, yield several points that correspond to states of equal enthalpy. We join these points with a smooth curve (called an *isenthalpic curve*).



Analysis of isenthalpic curve

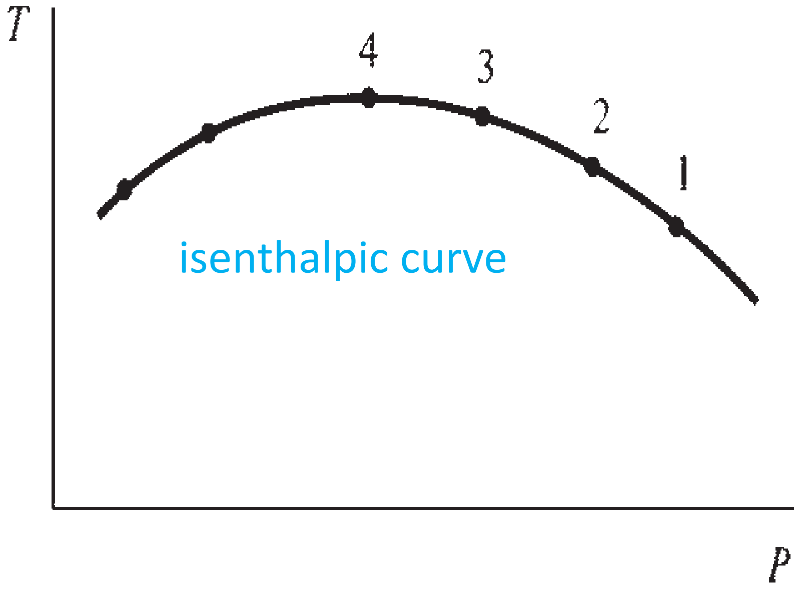
- The slope of this curve at any point gives $(\Delta T/\Delta P)_H$ for the temperature and pressure at that point.
- Values of T and P for which μ is negative (points to the right of point 4) correspond to warming on Joule–Thomson expansion.
- At point 4, μ is zero.
- To the left of point 4, μ is positive, and the gas is cooled by throttling.
- To generate further isenthalpic curves and get more values of μ (T, P), we use different initial temperatures T_1.

Values of μ for gases range from +3 to -0.1°C/atm, depending on the gas and on its temperature and pressure.



Joule–Thomson throttling for gas liquefaction

- Joule–Thomson throttling is used to liquefy gases. For a gas to be cooled by a Joule–Thomson expansion ($\Delta P < 0$), its μ must be positive over the range of T and P involved.
- In Joule–Thomson liquefaction of gases, the porous plug is replaced by a narrow opening (a needle valve).
- Another method of gas liquefaction is an approximately reversible adiabatic expansion against a piston.



Lecture-10

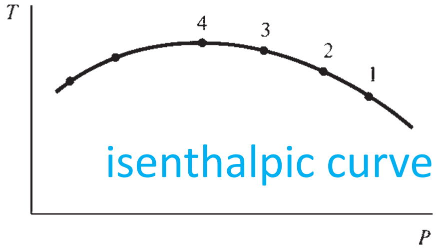
Contents

- Joule-Thomson coefficient and Inversion Temperature
- The application of the Joule–Thomson effect in Refrigerator
- Perfect gases and the first law
- Reversible Isothermal Process
- Reversible adiabatic process
- Assignment

Joule-Thomson coefficient and Inversion Temperature

We define the Joule–Thomson coefficient μ by

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$



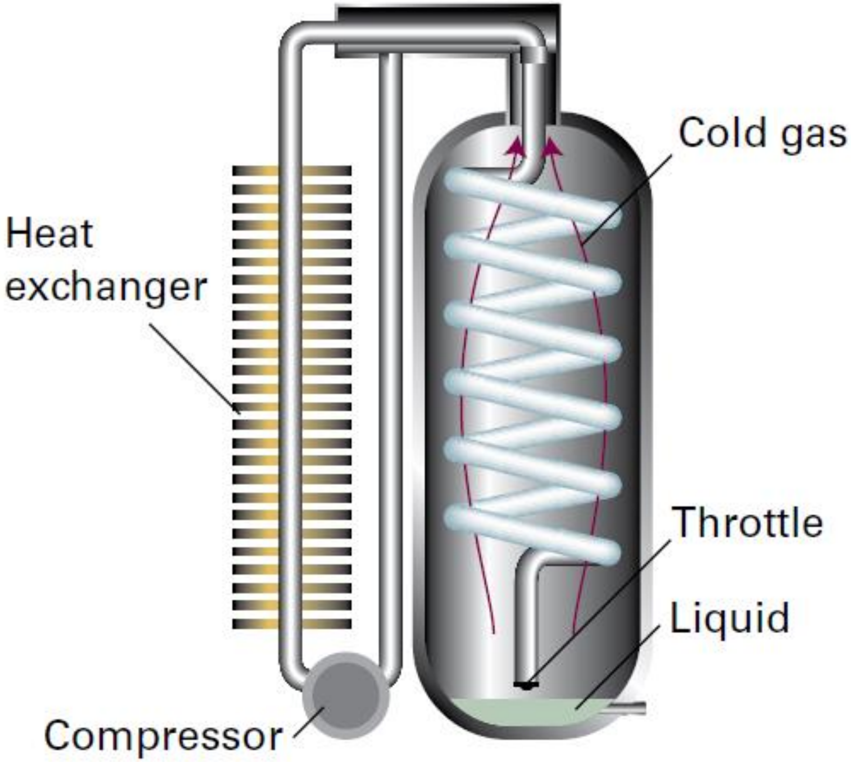
- If μ is positive, the gas cools on expansion; if μ is negative, the gas warms on expansion. The temperature at which the sign changes is called the **Inversion temperature.**

- Most gases have positive Joule-Thomson coefficients and hence they cool on expansion at room temperature.

- The inversion temperature for H_2 is –80ºC. Above the inversion temperature, μ is negative. Thus at room temperature hydrogen warms on expansion. Hydrogen must first be cooled below –80ºC (with liquid nitrogen) so that it can be liquefied by further Joule-Thomson expansion. So is the case with helium.

The application of the Joule–Thomson effect in Refrigerator

The principle of the Linde refrigerator is shown in this diagram. The gas is recirculated, and so long as it is beneath its inversion temperature it cools on expansion through the throttle. The cooled gas cools the high-pressure gas, which cools still further as it expands. Eventually liquefied gas drips from the throttle.



PERFECT GASES AND THE FIRST LAW

A perfect gas is one that obeys both the following equations:

$$\boxed{\begin{aligned} &PV = nRT \\ \text{and} \quad &(\partial U/\partial V)_T = 0 \end{aligned}}$$

For a closed system in equilibrium, the internal energy (and any other state function) can be expressed as a function of temperature and volume:

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

For a perfect gas, U is independent of volume. Therefore U of a perfect gas depends only on temperature:

$$\boxed{U = U(T)}$$

Since U is independent of V for a perfect gas, the partial derivative $(\partial U/ \partial T)_V$ for C_V becomes an ordinary derivative: $C_V = dU/dT$ *and*

$$\boxed{dU = C_V\, dT}$$

Therefore, C_V of a perfect gas depends only on T:

$$\boxed{C_V = C_V(T)}$$

For a perfect gas,

$$H = U + PV = U + nRT$$

As $U = U(T)$, H depends only on T for a perfect gas.

Since H is independent of P for a perfect gas, the partial derivative $(\partial H/\partial T)_P$ for C_P becomes an ordinary derivative: $C_P = dH/dT$ *and*

$$\boxed{dH = C_P\,dT}$$

Therefore, C_P of a perfect gas depends only on T:

$$C_P = C_P(T)$$

$$\mu_J C_V = -(\partial U/\partial V)_T$$

Since $(\partial U/\partial V)_T = 0, \qquad \mu_J = 0$

$$\mu \quad C_P = -(\partial H/\partial P)_T$$

Since, $(\partial H/\partial P)_T = 0, \quad \mu \quad = 0$

The first law, $dU = dq + dw$ (for closed system)

becomes, $dU = C_V\, dT = dq - P\, dV$

Reversible adiabatic process

- The temperature of a perfect gas falls when it does work in an adiabatic expansion.
- Work is done, but as no heat enters the system, the internal energy falls, and therefore the temperature of the working gas also falls.
- In molecular terms, the kinetic energy of the molecules falls as work is done, so their average speed decreases, and hence the temperature falls too.

The change in temperature

Deriving an expression for the temperature change in a reversible adiabatic expansion

The work done when the gas expands reversibly by dV is dw = $-p$dV.

For a perfect gas, dU = C_VdT

Equating these expressions for dU gives

$$C_V\mathrm{d}T = -p\mathrm{d}V$$

Because the gas is perfect, p can be replaced by nRT/V to give $C_V\mathrm{d}T = -(nRT/V)\mathrm{d}V$ and therefore

$$\frac{C_V\mathrm{d}T}{T} = -\frac{nR\mathrm{d}V}{V}$$

Integration of the expression gives the overall change

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

or, $$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

or, $$C_v ln \frac{T_f}{T_i} = -(C_p - C_v) ln \frac{V_f}{V_i}$$ [As C_p-C_v = nR]

or, $$ln \frac{T_f}{T_i} = -\left(\frac{C_p - C_v}{C_v}\right) ln \frac{V_f}{V_i}$$

or, $$ln \frac{T_f}{T_i} = -(\gamma - 1) ln \frac{V_f}{V_i}$$ [$\gamma = C_p/C_v$]

or, $$ln \frac{T_f}{T_i} = ln \left(\frac{V_i}{V_f}\right)^{\gamma-1}$$

or, $$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{\gamma-1} \quad (1)$$

or, $$T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1} \quad (2)$$

or, $$TV^{\gamma-1} = \text{Constant}$$

The change in pressure

The initial and final states of a perfect gas satisfy the perfect gas law regardless of how the change of state takes place, so $pV = nRT$ can be used to write

$$\frac{p_\mathrm{i}V_\mathrm{i}}{p_\mathrm{f}V_\mathrm{f}} = \frac{T_\mathrm{i}}{T_\mathrm{f}} \qquad (3)$$

From equations (1) and (3) it follows that

$$\frac{P_iV_i}{P_fV_f} = \left(\frac{V_f}{V_i}\right)^{\gamma-1}$$

or, $$\frac{P_i}{P_f} = \frac{V_f}{V_i} \times \left(\frac{V_f}{V_i}\right)^{\gamma-1}$$

or, $$\frac{P_i}{P_f} = \left(\frac{V_f}{V_i}\right)^{\gamma} \qquad (4)$$

or, $$\boxed{pV^{\gamma} = \text{Constant}}$$

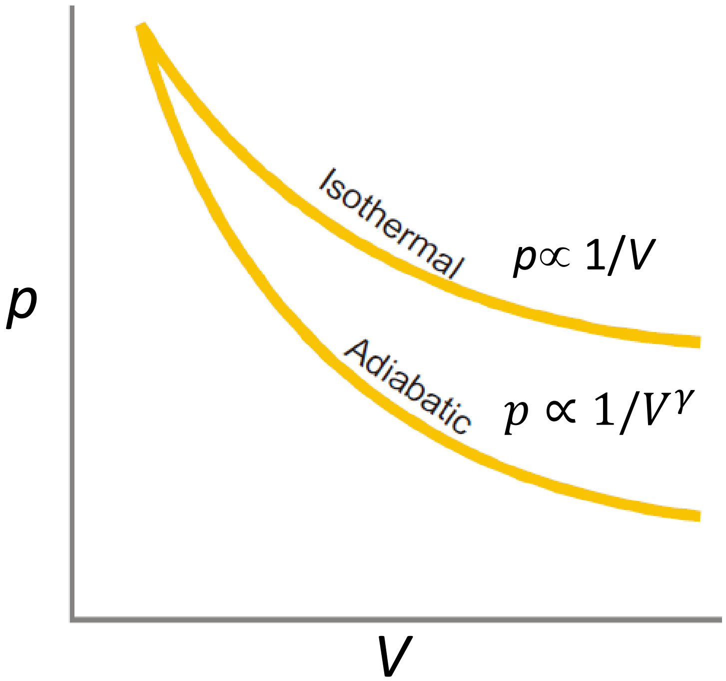
Comparison between Isothermal and Adiabatic Expansions

Pressure-volume relations of an ideal gas under isothermal conditions (T, constant) and adiabatic conditions are:

pV = constant (Isothermal)

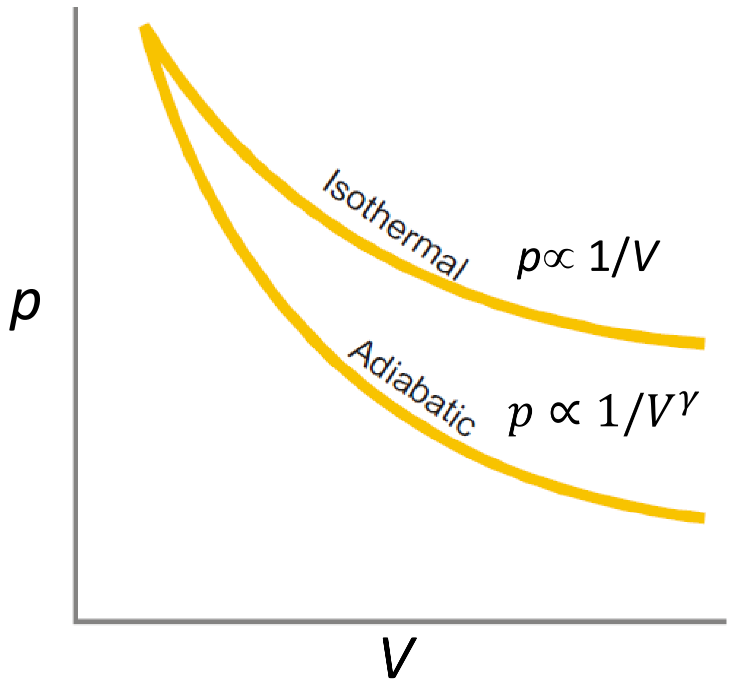
pV^{γ} = constant (Adiabatic)

- For a monatomic perfect gas, $\gamma = \frac{5}{3}$
- For a non-linear polyatomic molecule, $\gamma = \frac{4}{3}$



Comparison between Isothermal and Adiabatic Expansions

Because $\gamma > 1$, an adiabat falls more steeply ($p \propto 1/V^{\gamma}$) than the corresponding isotherm ($p \propto 1/V$).



The physical reason for the difference

In an isothermal expansion, energy flows into the system as heat and maintains the temperature. As a result, the pressure does not fall as much as in an adiabatic expansion.

Work done in adiabatic process

- From the first law of thermodynamics,

$$\Delta U = q + w$$

- For an adiabatic process, $q = 0$, it follows that $\Delta U = w_{\mathrm{ad}}$.
- Again, $\Delta U = C_{\mathrm{V}}\Delta T$
- By equating the two expressions for ΔU,

$$w_{\mathrm{ad}} = C_{\mathrm{V}}\Delta T$$

The work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states.

Assignment

- Compile important equations discussed in this chapter (First Law of Thermodynamics) mentioning related property.
- Write down the comments (if any).
- You may take help from Atkin′s Physical Chemistry, 11th edition.
- Short out the equations required to calculate q, w, ΔU and ΔH.

Checklist of concepts

☐ 1. **Work** is the process of achieving motion against an opposing force.

☐ 2. **Energy** is the capacity to do work.

☐ 3. An **exothermic process** is a process that releases energy as heat.

☐ 4. An **endothermic process** is a process in which energy is acquired as heat.

☐ 5. **Heat** is the process of transferring energy as a result of a temperature difference.

☐ 6. In molecular terms, work is the transfer of energy that makes use of organized motion of atoms in the surroundings and heat is the transfer of energy that makes use of their disorderly motion.

☐ 7. **Internal energy**, the total energy of a system, is a state function.

☐ 8. The internal energy increases as the temperature is raised.

☐ 9. The **equipartition theorem** can be used to estimate the contribution to the internal energy of each classically behaving mode of motion.

☐ 10. The **First Law** states that the internal energy of an isolated system is constant.

☐ 11. Free expansion (expansion against zero pressure) does no work.

☐ 12. A **reversible change** is a change that can be reversed by an infinitesimal change in a variable.

☐ 13. To achieve **reversible expansion**, the external pressure is matched at every stage to the pressure of the system.

☐ 14. The energy transferred as heat at constant volume is equal to the change in internal energy of the system.

☐ 15. **Calorimetry** is the measurement of heat transactions.

Checklist of concepts

☐ 1. Energy transferred as heat at constant pressure is equal to the change in **enthalpy** of a system.

☐ 2. Enthalpy changes can be measured in a constant-pressure calorimeter.

☐ 3. The **heat capacity at constant pressure** is equal to the slope of enthalpy with temperature.

Property	Equation	Comment
First Law of thermodynamics	$\Delta U = q + w$	Convention
Work of expansion	$\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V$	
Work of expansion against a constant external pressure	$w = -p_{\mathrm{ex}}\Delta V$	$p_{\mathrm{ex}} = 0$ for free expansion
Reversible work of expansion of a gas	$w = -nRT\ln(V_{\mathrm{f}}/V_{\mathrm{i}})$	Isothermal, perfect gas
Internal energy change	$\Delta U = q_V$	Constant volume, no other forms of work
Electrical heating	$q = It\Delta\phi$	
Heat capacity at constant volume	$C_V = (\partial U/\partial T)_V$	Definition

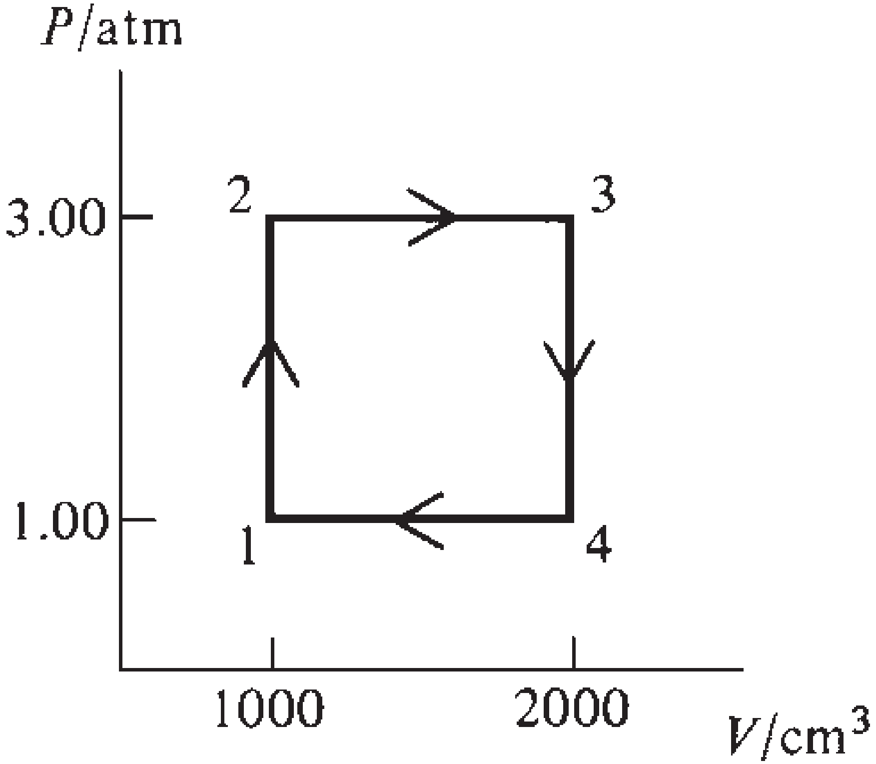
Property	Equation	Comment
Enthalpy	$H = U + pV$	Definition
Heat transfer at constant pressure	$\mathrm{d}H = \mathrm{d}q_p$, $\Delta H = q_p$	No additional work
Relation between ΔH and ΔU at a temperature T	$\Delta H = \Delta U + \Delta n_{\mathrm{g}}RT$	Molar volumes of the participating condensed phases are negligible
Heat capacity at constant pressure	$C_p = (\partial H/\partial T)_p$	Definition
Relation between heat capacities	$C_p - C_V = nR$	Perfect gas

Property	Equation	Comment
Change in $U(V,T)$	$\mathrm{d}U = (\partial U/\partial V)_T\mathrm{d}V + (\partial U/\partial T)_V\mathrm{d}T$	Constant composition
Internal pressure	$\pi_T = (\partial U/\partial V)_T$	Definition; for a perfect gas, $\pi_T = 0$
Change in $U(V,T)$	$\mathrm{d}U = \pi_T\mathrm{d}V + C_V\mathrm{d}T$	Constant composition
Expansion coefficient	$\alpha = (1/V)(\partial V/\partial T)_p$	Definition
Isothermal compressibility	$\kappa_T = -(1/V)(\partial V/\partial p)_T$	Definition
Relation between heat capacities	$C_p - C_V = nR$	Perfect gas
	$C_p - C_V = \alpha^2 TV/\kappa_T$	
Joule–Thomson coefficient	$\mu = (\partial T/\partial p)_H$	For a perfect gas, $\mu = 0$
Change in $H(p,T)$	$\mathrm{d}H = -\mu C_p\mathrm{d}p + C_p\mathrm{d}T$	Constant composition

Calculation of *q*, *w*, and ΔU

Suppose 0.100 mol of a perfect gas having $C_{V,m} = 1.50R$ independent of temperature undergoes the reversible cyclic process 1 → 2 → 3 → 4 → 1 shown in the figure, where either *P* or *V* is held constant in each step. Calculate *q*, *w*, and ΔU for each step and for the complete cycle.

Reversible cyclic process



Hints

- Since we know how P varies in each step and since the steps are reversible, we can readily find w for each step by integrating $dw_{\mathrm{rev}} = -P\,dV$.

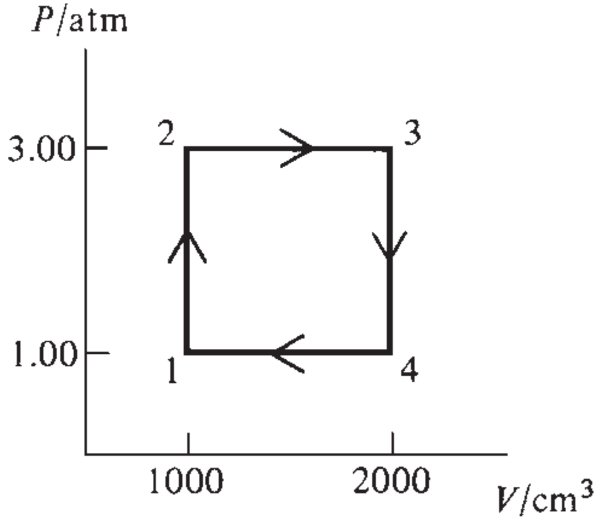
- Since either V or P is constant in each step, we can integrate $dq_V = C_V\,dT$ and $dq_P = C_P\,dT$ to find the heat in each step.

- The first law $\Delta U = q + w$ then allows calculation of ΔU.

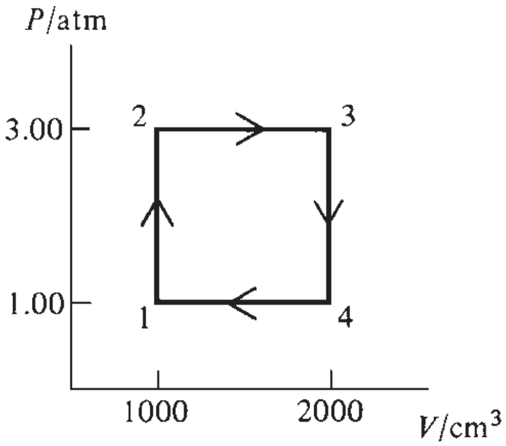
Calculation of *T*

- To evaluate integrals like $\int_1^2 C_V\,dT$, we will need to know the temperatures of states 1, 2, 3, and 4. We therefore begin by using $PV = nRT$ to find these temperatures.

- For example, $T_1 = P_1V_1/nR = 122$ K. Similarly, $T_2 = 366$ K, $T_3 = 732$ K, $T_4 = 244$ K.



Calculation of *w*



- Step 1 → 2 is at constant volume, no work is done, and $w_{1\to2} = 0$.
- Step 2→3 is at constant pressure, and

$$w_{2\to3} = -\int_2^3 P\,dV = -P(V_3 - V_2)$$

$$= -(3.00\text{ atm})(2000\text{ cm}^3 - 1000\text{ cm}^3)$$

$$= -3000\text{ cm}^3\text{ atm}\,(8.314\text{ J})/(82.06\text{ cm}^3\text{ atm}) = -304\text{ J}$$

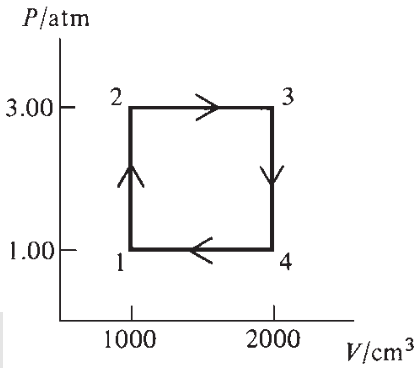
where two values of *R* were used to convert to joules.

- Similarly, $w_{3\to4} = 0$ and $w_{4\to1} = 101$ J.

The work w for the complete cycle is the sum of the works for the four steps, so

$$w = -304\text{ J} + 0 + 101\text{ J} + 0 = -203\text{ J}$$

Calculation of *q*



- Step 1 → 2 is at constant volume, and

$$q_{1\to2} = \int_1^2 C_V\,dT = nC_{V,\mathrm{m}}\int_1^2 dT = n(1.50R)(T_2 - T_1)$$

$$= (0.100\ \mathrm{mol})1.50[8.314\ \mathrm{J/(mol\ K)}](366\ \mathrm{K} - 122\ \mathrm{K}) = 304\ \mathrm{J}$$

- Step 2 → 3 is at constant pressure, and $q_{2\to3} = \int_2^3 C_P\,dT$.

  We have, $C_{P,\mathrm{m}} = C_{V,\mathrm{m}} + R = 2.50R$

  Applying similar operation we find $q_{2\to3}$ = 761 J.

- Similarly, $q_{3\to4}$ = -608.5 J and $q_{4\to1}$ = -253.5 J.

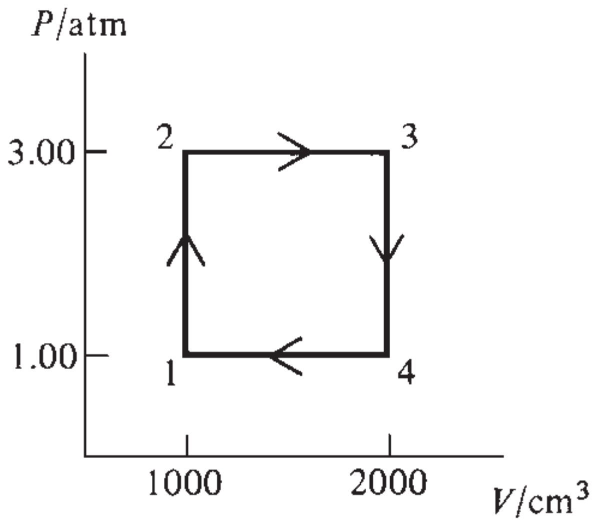
The total heat for the cycle is

q = 304 J + 761 J – 608.5 J – 253.5 J = 203 J

Calculation of ΔU

- $\Delta U_{1\to2} = q_{1\to2} + w_{1\to2} = 304\text{ J} + 0 = 304\text{ J}$

- Similarly we find,



$\Delta U_{2\to3} = 457\text{ J}$

$\Delta U_{3\to4} = -608.5\text{ J}$

$\Delta U_{4\to1} = -152.5\text{ J}$

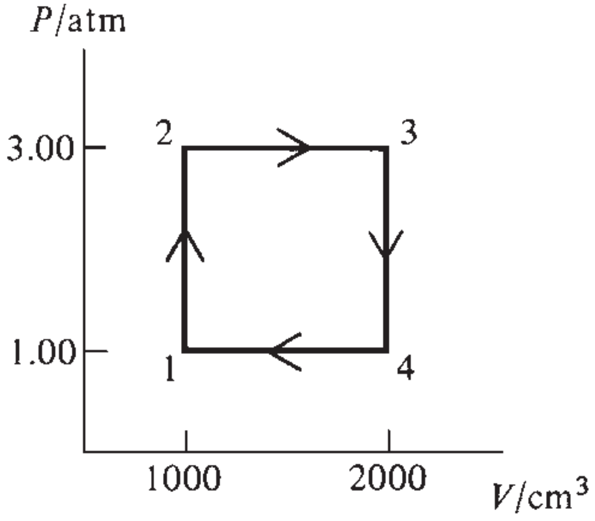
For the complete cycle,

$\Delta U = 304\text{ J} + 457\text{ J} - 608.5\text{ J} - 152.5\text{ J} = 0$

For this cyclic process, we found $\Delta U = 0$, $q \neq 0$, and $w \neq 0$. These results are consistent with the fact that U is a state function but q and w are not.

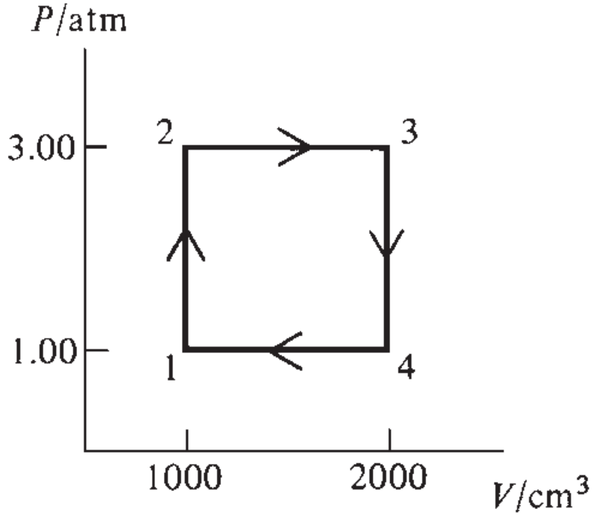
Exercise **1**

Suppose 0.100 mol of a perfect gas having $C_{V,m}$ = 1.50R . Use the perfect-gas equation $dU = C_V$ dT to find ΔU for each step and for complete cycle of the figure.



$$\Delta U_{1\to 2} = \int_1^2 C_V dT = C_V(T_2 - T_1)$$
$$= nC_{V,m}(T_2 - T_1) = 0.100\,\text{mol} \times 1.50R(366\,\text{K} - 122\,\text{K})$$
$$= 0.100\,\text{mol} \times 1.50 \times 8.314\,\text{J K}^{-1}\text{mol}^{-1} \times (366\,\text{K} - 122\,\text{K})$$
$$= 304\,\text{J}$$

Similarly we find,



$$\Delta U_{2\to 3} = 457\text{ J}$$

$$\Delta U_{3\to 4} = -608.5\text{ J}$$

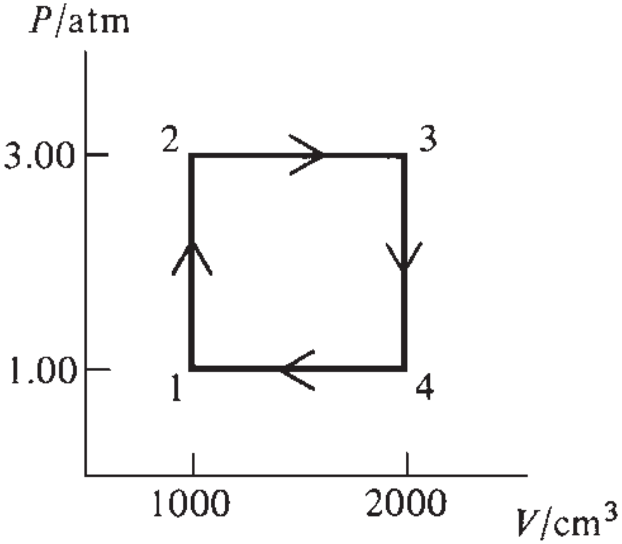
$$\Delta U_{4\to 1} = -152.5\text{ J}$$

For the complete cycle,

$\Delta U = 304\text{ J} + 457\text{ J} - 608.5\text{ J} - 152.5\text{ J} = 0$

Exercise **2**

Suppose 0.100 mol of a perfect gas having $C_{V,m} = 1.50R$. Calculate *w* for each step and for the complete cycle. Verify that *w* for this reversible cyclic process equals minus the area enclosed by the lines in the figure.



Exercise **2**

Answer Hints

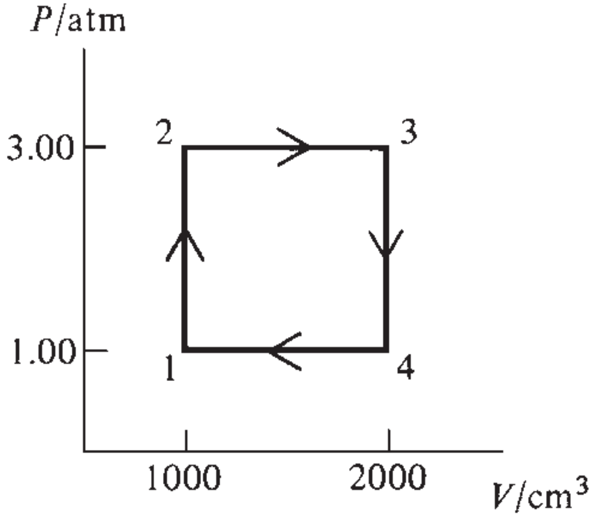
- Calculate *T* for each state
- Calculate *w* for each step
- Calculate *w* for complete cycle
- Calculate area enclosed by the lines
- Comment

Area enclosed by the lines = $\Delta P \times \Delta V$

= 2.00 atm × 1000 cm^3

= 2.00 atm × 1000 cm^3 ×(8.314 J/ 82.06 cm^3 atm)

= 203 J



Reversible Isothermal Process in a Perfect Gas

- Consider the special case of a reversible isothermal (constant-*T*) process in a perfect gas.
- For a fixed amount of a perfect gas, *U* depends only on *T* .
- Therefore $\Delta U = 0$ for an isothermal change of state in a perfect gas.
- This also follows from $dU = C_V\, dT$ for a perfect gas.
- The first law $\Delta U = q + w$ becomes $0 = q + w$ and $q = -w$.

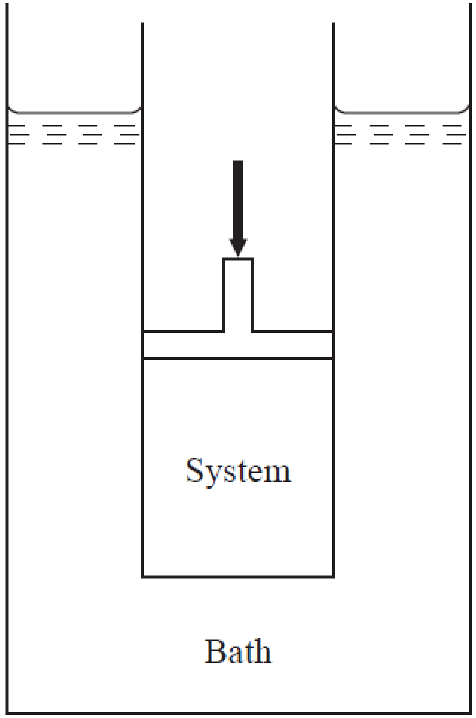


Figure 2.11

Setup for an isothermal volume change.

Integration of $dw_{\text{rev}} = -P\,dV$ and use of $PV = nRT$ give

$$w = -\int_1^2 P\,dV = -\int_1^2 \frac{nRT}{V}\,dV$$

$$= -nRT\int_1^2 \frac{1}{V}\,dV = -nRT(\ln V_2 - \ln V_1)$$

$$w = -q = nRT\ln\frac{V_1}{V_2} = nRT\ln\frac{P_2}{P_1}$$

Worked Example

A cylinder fitted with a frictionless piston contains 3.00 mol of He gas at P =1.00 atm and is in a large constant-temperature bath at 400 K. The pressure is reversibly increased to 5.00 atm. Find w, q, and ΔU for this process.

- It is an excellent approximation to consider the helium as a perfect gas.
- Since T is constant, $\Delta U = 0$.
- $w = nRT \ln (P_2/P_1)$

$$= (3.00 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(400\text{K}) \ln(5.00/1.00)$$
$$= (9980 \text{ J}) \ln 5.00 = (9980 \text{ J}) (1.609)$$
$$= 1.61\times 10^4 \text{ J}$$

- Also, $q = -w = -1.61\times10^4$ J.
- Of course, w is positive for the compression.
- The heat q is negative because heat must flow from the gas to the surrounding constant-temperature bath to maintain the gas at 400 K as it is compressed.

Exercise

0.100 mol of a perfect gas with $C_{V,\mathrm{m}} = 1.50R$ expands reversibly and isothermally at 300 K from 1.00 to 3.00 L. Find q, w, and ΔU for this process. (*Answer*: 274 J, -274 J, 0.)

Lecture-11

Contents

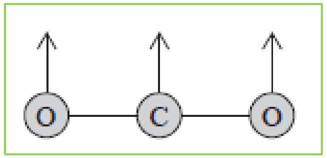
The molecular nature of internal energy

- Translational energy
- Rotational energy
- Vibrational energy
- Electronic energy
- Intermolecular forces

A qualitative understanding of molecular energies

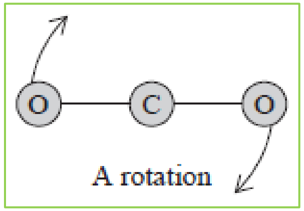
Consider first a gas. The molecules are moving through space.

Translational kinetic energy



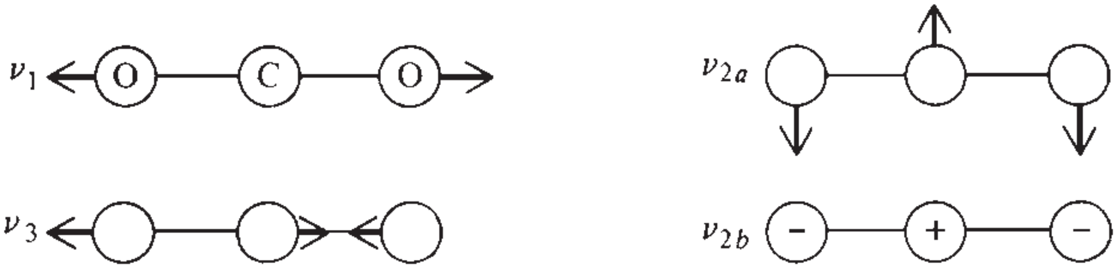
- A molecule has a translational kinetic energy $\frac{1}{2}mv^2$, where m and v are the mass and speed of the molecule.
- A **translation** is a motion in which every point of the body moves the same distance in the same direction.
- The total molecular translational kinetic energy $U_{\mathrm{tr,m}}$ of one mole of a gas is directly proportional to the absolute temperature and is given by $U_{\mathrm{tr,m}} = \frac{3}{2}RT$, where R is the gas constant.

Rotational Energy

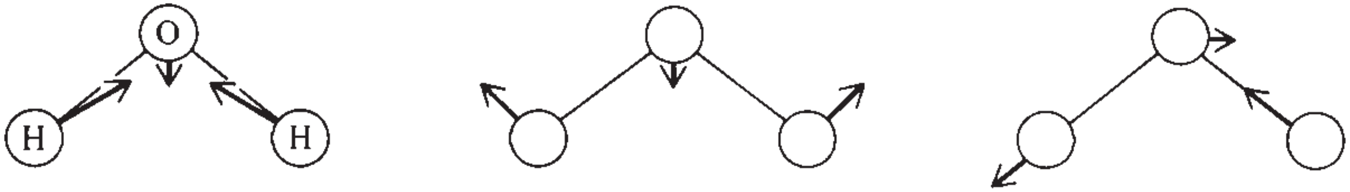


- If each gas molecule has more than one atom, then the molecules undergo rotational and vibrational motions in addition to translation.
- A **rotation** is a motion in which the spatial orientation of the body changes, but the distances between all points in the body remain fixed and the center of mass of the body does not move (so that there is no translational motion).
- Except at very low temperatures the energy of molecular rotation $U_{\text{rot,m}}$ in one mole of gas is RT for linear molecules and $\frac{3}{2}RT$ for nonlinear molecules: $U_{\text{rot,lin,m}} = RT$; $U_{\text{rot,nonlin,m}} = \frac{3}{2}RT$.

Vibrational Energy



Normal vibrational modes of CO_2. The plus and minus signs indicate motion out of and into the plane of the paper



$\tilde{\nu}_1 = 3657\ \mathrm{cm}^{-1}$ $\tilde{\nu}_2 = 1595\ \mathrm{cm}^{-1}$ $\tilde{\nu}_3 = 3756\ \mathrm{cm}^{-1}$

The normal modes of H_2O. The heavy oxygen atom has a much smaller vibrational amplitude than the light hydrogen atoms.

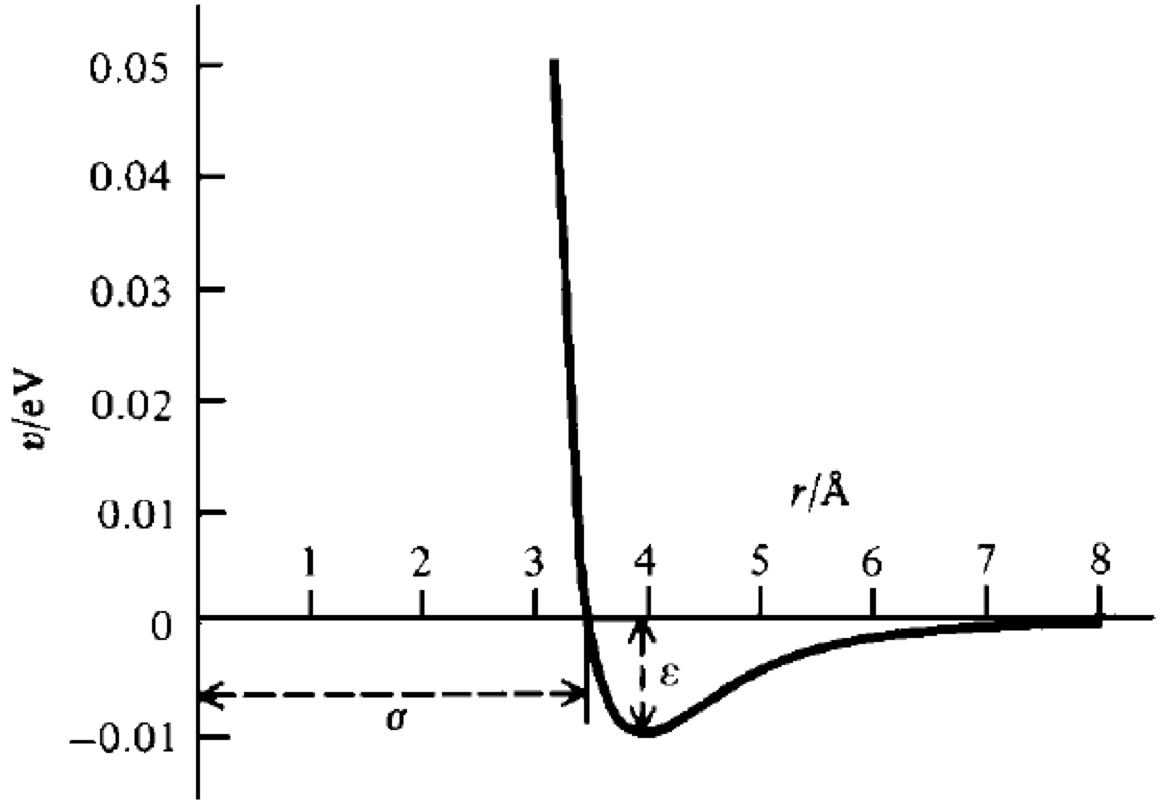
- In a molecular **vibration,** the atoms oscillate about their equilibrium positions in the molecule. A molecule has various characteristic ways of vibrating, each way being called a vibrational normal mode.
- Quantum mechanics shows that the lowest possible vibrational energy is not zero but is equal to a certain quantity called the molecular zero-point vibrational energy. The vibrational energy contribution U_{vib} to the internal energy of a gas is a complicated function of temperature.
- For most light diatomic (two-atom) molecules at low and moderate temperatures (up to several hundred kelvins), the average molecular vibrational energy remains nearly fixed at the zero-point energy as the temperature increases. For polyatomic molecules and for heavy diatomic molecules at room temperature, the molecules usually have significant amounts of vibrational energy above the zero-point energy.

Electronic energy

Besides translational, rotational, and vibrational energies, a molecule possesses **electronic energy** $\varepsilon_{el} = \varepsilon_{eq} - \varepsilon_{\infty,}$ where ε_{eq} is the energy of the molecule with the nuclei at rest (no translation, rotation, or vibration) at positions corresponding to the equilibrium molecular geometry, and ε_{∞} is the energy when all the nuclei and electrons are at rest at positions infinitely far apart from one another, so as to make the electrical interactions between all the charged particles vanish.

Intermolecular forces

- Besides translational, rotational, vibrational, and electronic energies, the gas molecules possess energy due to attractions and repulsions between them **(intermolecular forces);** intermolecular attractions cause gases to liquefy.
- The force between two molecules depends on the orientation of one molecule relative to the other. For simplicity, one often ignores this orientation effect and uses a force averaged over different orientations so that it is a function solely of the distance r between the centers of the interacting molecules.



The Lennard-Jones intermolecular potential for Ar.

Additional Slides

For a gas or liquid, the molar internal energy is

$$U_{\mathrm{m}} = U_{\mathrm{tr,m}} + U_{\mathrm{rot,m}} + U_{\mathrm{vib,m}} + U_{\mathrm{el,m}} + U_{\mathrm{intermol,m}} + U_{\mathrm{rest,m}}$$

where $U_{\mathrm{rest,m}}$ is the molar rest-mass energy of the electrons and nuclei, and is a constant.

Mathematical Background

Physical chemistry uses calculus extensively. Therefore, some ideas of differential calculus is reviewed in this lecture.

Functions and Limits

- To say that the variable y is a **function** of the variable x means that for any given value of x there is specified a value of y; we write $y = f(x)$.

- The variable x is called the *independent variable* or the *argument* of the function f, and y is the *dependent variable*. Instead of $y=f(x)$, one often writes $y=y(x)$.

To say that the limit of the function $f(x)$ as x approaches the value a is equal to c [which is written as $lim_{x \to a} f(x)=c$] means that for all values of x sufficiently close to a (but not necessarily equal to a) the difference between $f(x)$ and c can be made as small as we please.

Derivatives

Let $y = f(x)$.

Let the independent variable change its value from x to $x + h$;

This will change y from $f(x)$ to $f(x + h)$.

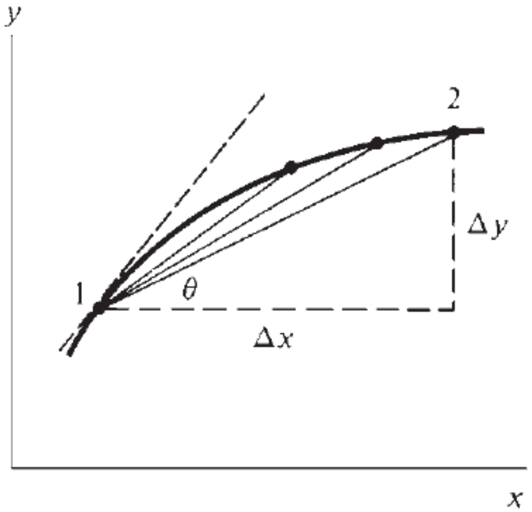
The average rate of change of y with x is

$$\boxed{\frac{\Delta y}{\Delta x} = \frac{f(x + h) - f(x)}{(x + h) - x} = \frac{f(x + h) - f(x)}{h}}$$

The *instantaneous* rate of change of y with x is the limit of this average rate of change taken as the change in x goes to zero.

The *instantaneous* rate of change is called the **derivative** of the function *f* and is symbolized by *f '*:

$$f'(x) \equiv \lim_{h\to 0}\frac{f(x+h)-f(x)}{h} = \lim_{\Delta x\to 0}\frac{\Delta y}{\Delta x}$$



The derivative of the function y = *f(x)* at a given point is equal to the slope of the curve of *y* versus *x* at that point.

As point 2 approaches point 1, the quantity $y/x = \tan\theta$ approaches the slope of the tangent to the curve at point 1.

The symbol ≡ indicates a definition.

As a simple example, let $y = x^2$. *Then*

$$f'(x) = \lim_{h \to 0} \frac{(x + h)^2 - x^2}{h}$$

$$= \lim_{h \to 0} \frac{2xh + h^2}{h} = \lim_{h \to 0} (2x + h) = 2x$$

The derivative of x^2 *is* $2x$.

An infinitesimally small change in x, *is* symbolize by dx. Denoting the corresponding infinitesimally small change in y by dy, we have,

$$dy = y'(x)\, dx$$

The quantities dy and dx are called **differentials.** Above equation gives the alternative notation dy/dx for a derivative.

Partial Derivatives

Let *z* be a function of *x* and *y; z =f(x, y).*We define the **partial derivative** of *z* with respect to *x* as

$$\left(\frac{\partial z}{\partial x}\right)_y \equiv \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x}$$

The **partial derivative** of *z* with respect to *y* at constant *x is*

$$\left(\frac{\partial z}{\partial y}\right)_x \equiv \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y}$$

There may be more than two independent variables. For example, let *z* = *g(w, x, y)*. The partial derivative of *z* with respect to *x* at constant w and *y* is

$$\left(\frac{\partial z}{\partial x}\right)_{w,y} \equiv \lim_{\Delta x \to 0} \frac{g(w, x + \Delta x, y) - g(w, x, y)}{\Delta x}$$