THERMODYNAMICS

Thermodynamics is the study of the various properties and, particularly, the relations between the various properties of systems in equilibrium. It is primarily an experimental science that was developed in the 1800s and still is of great practical value in many fields, such as chemistry, biology, geology, physics, and engineering. For example, we will use thermodynamics to show the quantitative relationship between the vapor pressure of a liquid and its heat of vaporization, or to show that if a gas obeys the equation of state $P\overline{V} = RT$, then its energy depends only upon its temperature. One of the most important and fruitful applications of thermodynamics is the analysis of chemical equilibria, where thermodynamics can be used to determine the temperature and pressure that optimize the products of a given chemical reaction. No industrial process would ever be undertaken without a thorough thermodynamic analysis of the chemical reactions involved.

All the results of thermodynamics are based on three fundamental laws. These laws summarize an enormous body of experimental data, and there are absolutely no known exceptions. In fact, Einstein said of thermodynamics:

> A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore, the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.[1]

Einstein's assessment is worth comment. Realize that thermodynamics was developed in the 1800s before the atomic theory of matter was generally accepted. The laws and results of thermodynamics are not based on any atomic or molecular theory; they

are independent of atomic and molecular models. The development of thermodynamics along these lines is called *classical thermodynamics*. This character of classical thermodynamics is both a strength and a weakness. We can be assured that classical thermodynamic results will never need to be modified as our knowledge of atomic and molecular structure improves, but classical thermodynamics gives us only a limited insight at the molecular level.

With the development of atomic and molecular theories in the late 1800s and early 1900s, thermodynamics was given a molecular interpretation, or a molecular basis. This field is called *statistical thermodynamics* because it relates averages of molecular properties to macroscopic thermodynamic properties such as temperature or pressure.

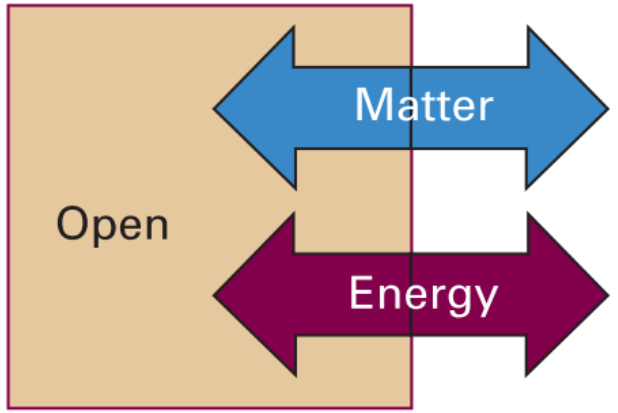
The First Law of Thermodynamics is the law of conservation of energy applied to macroscopic systems. To present the first law, we must introduce the concepts of work and heat as they are used in thermodynamics. As we will see in the next section, work and heat are modes of energy transfer between a system and its surroundings.

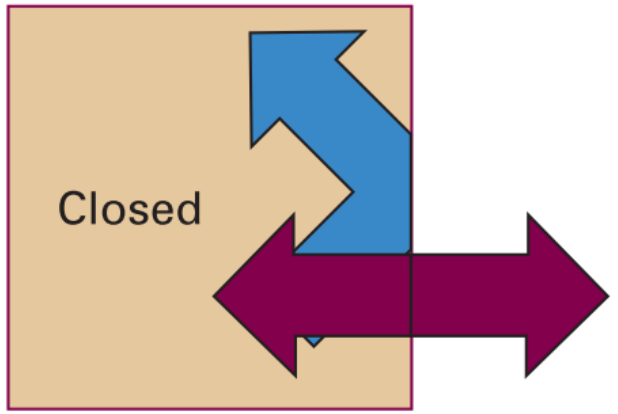
What do we study in chemical thermodynamics?

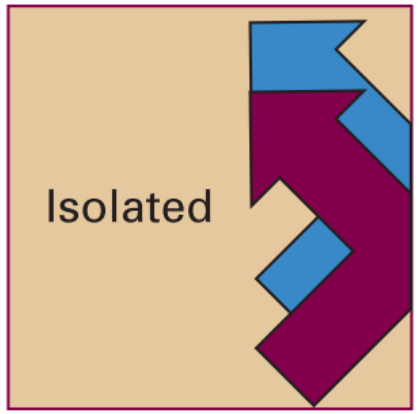
Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air. The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell. Thus, various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state.

Some Basic Concepts and Terminology

For the purposes of thermodynamics, the universe is divided into two parts, the **system** and its **surroundings**. 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. The surroundings comprise the region outside the system and are where we make our measurements. The type of system depends on the characteristics of the boundary that divides it from the surroundings If matter can be transferred through the boundary between the system and its surroundings the system is classified as **open**. If matter cannot pass through the boundary the system is classified as **closed**. Both open and closed systems can exchange energy with their surroundings. For example, a closed system can expand and thereby raise a weight in the surroundings; a closed system may also transfer energy to the surroundings if they are at a lower temperature. An **isolated system** is a closed system that has neither mechanical nor thermal contact with its surroundings.







Some Basic Concepts and Terminology

Macroscopic Properties. The properties associated with a macroscopic system (i.e., consisting of large number of particles)· are called macroscopic properties. They are pressure, volume, temperature, composition, density. viscosity, surface tension, refractive index, etc.

Homogeneous and Heterogeneous Systems. A system is said to be homogeneous when it is Completely uniform throughout, as for example, a pure solid or a liquid or a solution or a mixture of gases. In other words, a homogeneous system consists of only one phase.

A **phase** is defined as a homogeneous physically distinct part of a system which is bounded by a surface and is mechanically separable from other parts of the system. A system is said to be heterogeneous when it is not uniform throughout. In other words, a heterogeneous system is one which consists of two or more phases. Thus a system consisting of two or more immiscible liquids, or a solid in contact with a liquid in which it does not dissolve, is a heterogeneous system. A liquid in contact with its vapour is also a heterogeneous system because it consists of two phases.

Some Basic Concepts and Terminology

State of a System: When the macroscopic properties of a system have definite values, the system is said to be in definite state. Whenever there is a change in any one of the macroscopic properties, the system is said to change into a different state. Thus, the state of a system is fixed by its macroscopic properties.

State Variables: Since the state of a system changes with change in any of the macroscopic properties, these properties are called state variables. It also follows that when a system changes from one state (called initial state) to another state (called final state), there is invariably a change in one or more of the macroscopic properties. Pressure temperature, volume, mass and composition are the most important state variables. In actual practice, it is not necessary to specify the state variables because some of them are interdependent. In the case of a single gas, composition is not one of the variables because it remains always 100 per cent. Further, if the gas is ideal and one mole of the gas is under examination, it obeys the equation PV=RT, where R is the gas constant. Evidently, if only two of the three variables (P, V and T) are known; the third can easily be calculated. The two variables, generally specified are temperature and pressure. These are called independent variables. The third variable, generally, volume is said to be dependent variable, as its value depends upon the values of P and T. Thus, the thermodynamic state of a system consisting of a single gaseous substance may be completely defined by specifying any two of the three variables, viz.; temperature, pressure and volume.

Some Basic Concepts and Terminology

Extensive and intensive properties; An extensive property of a system is that which depends upon the amount of the substance or substances present in the system. The examples are mass, volume and energy. An intensive property of a system is that which is independent of the amount of the substance present in the system. The examples are temperature, pressure, density ,viscosity, refractive index, surface tension and specific heat. In the light of the above definitions, extensive properties of a single (pure) substance will depend upon the number of moles (n) of the substance present and also on any two of the three variables P, V and T (called independent variables). If n is kept constant, the extensive properties of the system will depend only on the two independent variables.

Thermodynamic Processes; The operation by which a system changes from one state to another is called a process. Whenever a system changes from one state to another it is accompanied by change in energy. In the case of open systems, there may be change of matter as well. The following types of processes are known.

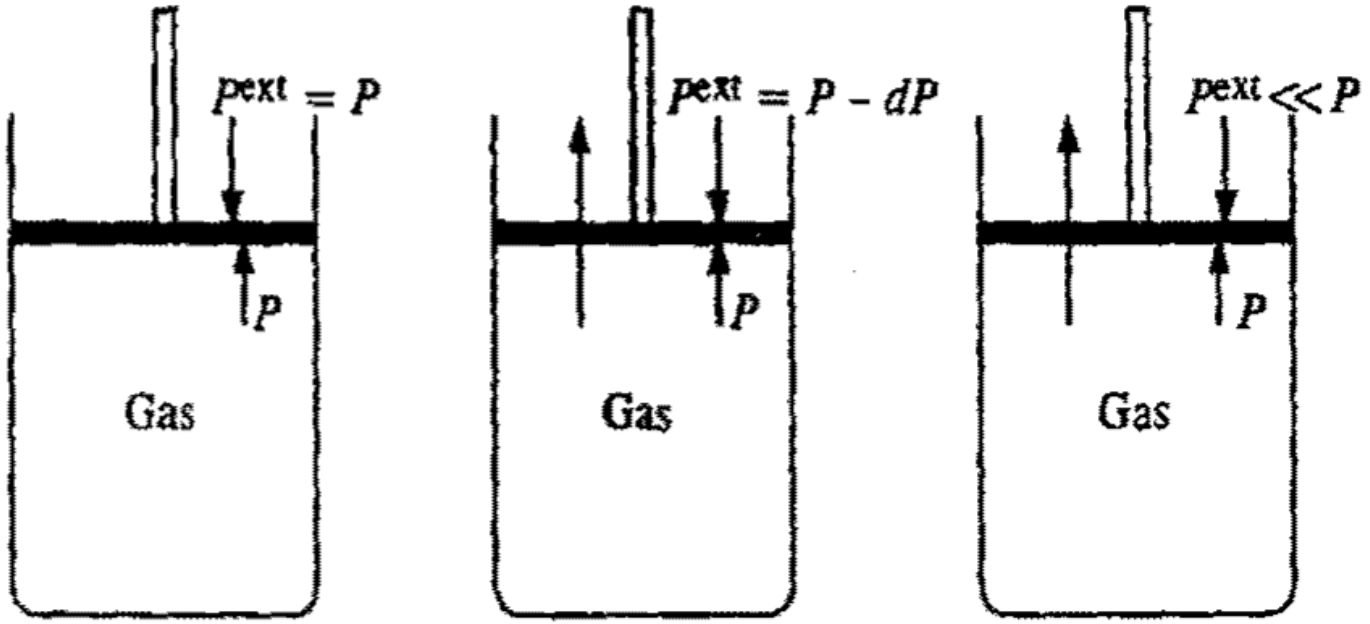
Isothermal process; A process is said to be isothermal if the temperature of the system remains constant during each 'stage of the process.

Adiabatic process; A process is said to be adiabatic if no heat enters or leaves the system during any step of the process.

Isobaric process; A process is said to be isobaric if the pressure of the system remains constant during each step of the process.

Some Basic Concepts and Terminology

Reversible and Irreversible Processes. A process carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force, is called a reversible process. Any process which does not take place in the above manner, i.e., a process which does not take place infinitesimally slowly, is said to be an Irreversible process. A reversible process cannot be realised in practice because it would require infinite time for its completion. Hence, almost all processes occurring in nature or laboratory are irreversible. A reversible process, therefore, remains imaginary and theoretical. Nevertheless, this concept is highly useful since it leads to some definite conclusions.



Reversible and irreversible expansion of a gas.

Work, Heat and Energy

The fundamental physical property in thermodynamics is work: work is done to achieve motion against an opposing force. A simple example is the process of raising a weight against the pull of gravity. A process does work if, in principle, it can be harnessed to raise a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston: the motion of the piston can in principle be used to raise a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be passed through a motor and used to raise a weight. The energy of a system is its capacity to do work. When work is done on an otherwise isolated system (for instance, by compressing a gas or winding a spring), the capacity of the system to do work is increased; in other words, the energy of the system is increased. When the system does work (when the piston moves out or the spring unwinds), the energy of the system is reduced and it can do less work than before.

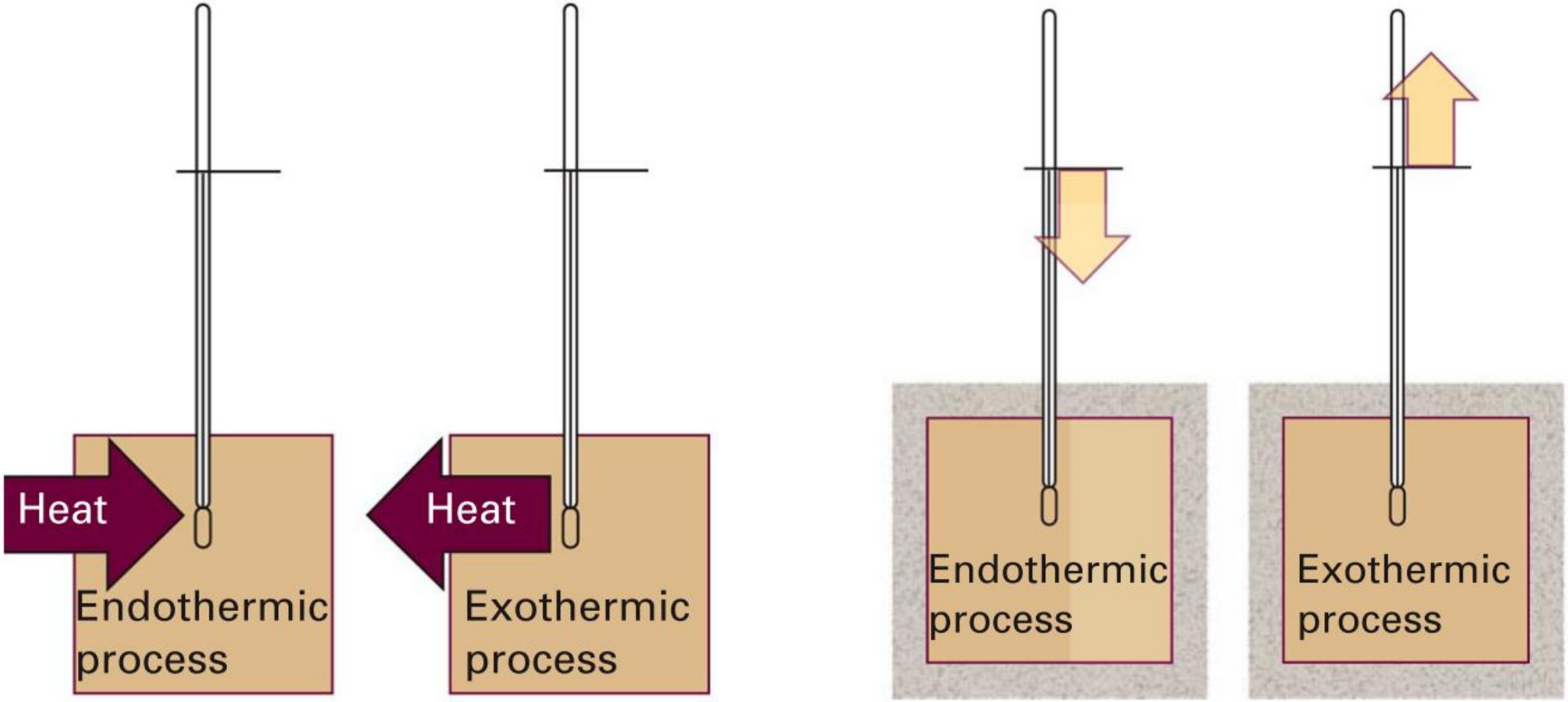
Experiments have shown that the energy of a system may be changed by means other than work itself. When the energy of a system changes as a result of a temperature difference between the system and its surroundings we say that energy has been transferred as heat.

Work, Heat and Energy

When a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than the same amount of cold water. Not all boundaries permit the transfer of energy even though there is a temperature difference between the system and its surroundings. Boundaries that do permit the transfer of energy as heat are called diathermic; those that do not are called adiabatic. An exothermic process is a process that releases energy as heat into its surroundings. All combustion reactions are exothermic. An endothermic process is a process in which energy is acquired from its surroundings as heat. An example of an endothermic process is the vaporization of water. In an exothermic process energy is transferred 'as heat' to the surroundings and in an endothermic process energy is transferred 'as heat' from the surroundings into the system. However, it must never be forgotten that heat is a process (the transfer of energy as a result of a temperature difference), not an entity. An endothermic process in a diathermic container results in energy flowing into the system as heat to restore the temperature to that of the surroundings.

Work, Heat and Energy

An exothermic process in a similar diathermic container results in a release of energy as heat into the surroundings. When an endothermic process takes place in an adiabatic container, it results in a lowering of temperature of the system; an exothermic process results in a rise of temperature.



Heat and Work: Molecular Interpretation

In molecular terms, heating is the transfer of energy that makes use of disorderly molecular motion in the surroundings. The disorderly motion of molecules is called thermal motion. The thermal motion of the molecules in the hot surroundings stimulates the molecules in the cooler system to move more vigorously and, as a result, the energy of the system is increased. When a system heats its surroundings, molecules of the system stimulate the thermal motion of the molecules in the surroundings

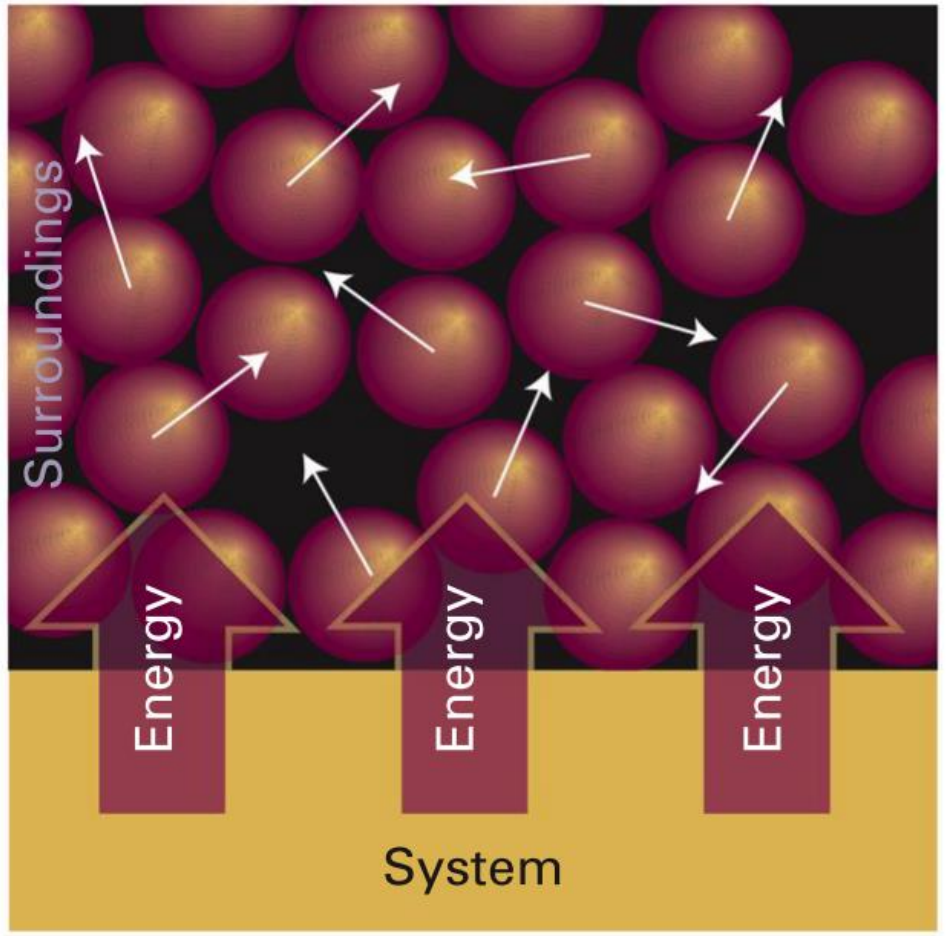


Fig: When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

Heat and Work: Molecular Interpretation

In contrast, work is the transfer of energy that makes use of organized motion in the surroundings. When a weight is raised or lowered, its atoms move in an organized way (up or down). The atoms in a spring move in an orderly way when it is wound; the electrons in an electric current move in an orderly direction. When a system does work it causes atoms or electrons in its surroundings to move in an organized way. Likewise, when work is done on a system, molecules in the surroundings are used to transfer energy to it in an organized way, as the atoms in a weight are lowered or a current of electrons is passed.

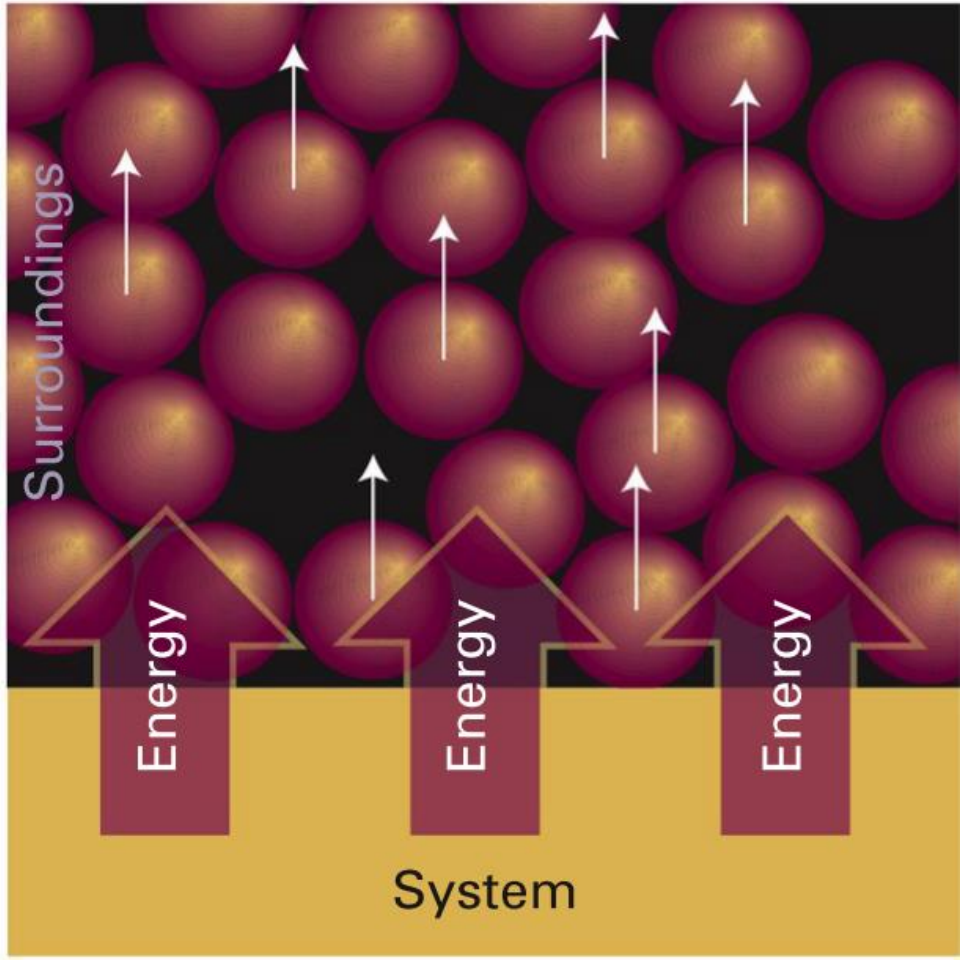


Fig: When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

Heat and Work: Molecular Interpretation

The distinction between work and heat is made in the surroundings. The fact that a falling weight may stimulate thermal motion in the system is irrelevant to the distinction between heat and work: work is identified as energy transfer making use of the organized motion of atoms in the surroundings, and heat is identified as energy transfer making use of thermal motion in the surroundings. In the adiabatic compression of a gas, for instance, work is done on the system as the atoms of the compressing weight descend in an orderly way, but the effect of the incoming piston is to accelerate the gas molecules to higher average speeds. Because collisions between molecules quickly randomize their directions, the orderly motion of the atoms of the weight is in effect stimulating thermal motion in the gas. We observe the falling weight, the orderly descent of its atoms, and report that work is being done even though it is stimulating thermal motion.

Pressure-Volume Work

Both work and heat refer to the manner in which energy is transferred between some system of interest and its surroundings. We define heat, q, to be the manner of energy transfer that results from a temperature difference between the system and its surroundings. Heat input to a system is considered a positive quantity; heat evolved by a system is considered a negative quantity. We define work, w, to be the transfer of energy between the system of interest and its surroundings as a result of the existence of unbalanced forces between the two. If the energy of the system is increased by the work, we say that work is done on the system by the surroundings, and we take it to be a positive quantity. On the other hand, if the energy of the system is decreased by the work, we say that the system does work on the surroundings, or that work is done by the system, and we take it to be a negative quantity. A common example of work in physical chemistry occurs during the expansion or compression of a gas as a result of the difference in pressures exerted by the gas and on the gas.

Pressure-Volume Work

An important aspect of work is that it can always be related to the raising or lowering of a mass in the surroundings. To see the consequences of this statement, consider the situation in Figure 1, where a gas is confined to a cylinder that exerts a force Mg on the gas. In Figure 1a, the initial pressure of the gas, Pi' is sufficient to push the piston upward, so there are pins holding it in position. Now, remove the pins and allow the gas to lift the mass upward to the new position shown, and let the pressure of the gas now be Pr. In this process, the mass M has been raised a distance h, so the work done by the system is

$$w = -Mgh$$

The negative sign here is in accord with our convention that work done by a system is taken to be a negative quantity. If we divide Mg by A, the area of the piston, and multiply h by A, then we have

$$w = -\frac{Mg}{A} \cdot Ah$$

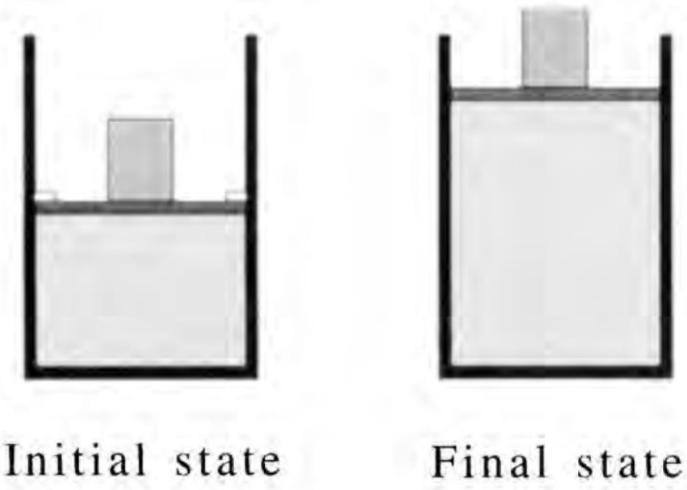


Fig. 1a: *The effect of work is equivalent to the raising or lowering of a mass in the surroundings. In (a) work is done by the system because the mass is raised,*

Pressure-Volume Work

But Mg/A is the external pressure exerted on the gas and Ah is the change in volume experienced by the gas, so we have

$$w = -P_{ext}\Delta V \qquad 1$$

Note that $\Delta V > 0$ in an expansion, so $w < 0$. Clearly, the external pressure must be less than the pressure of the initial state of the gas in order that the expansion occur.

After the expansion, $P_{ext} = P_f$

Now consider the situation in Figure **1b**, where the initial pressure of the gas is less than the external pressure $P_{ext} = Mg/A$, so the gas is compressed when the pins are removed. In this case, the mass M is lowered a distance h, and the work is given by

$$w = -Mgh = -\frac{Mg}{A}(Ah) = -P_{ext}\Delta V$$

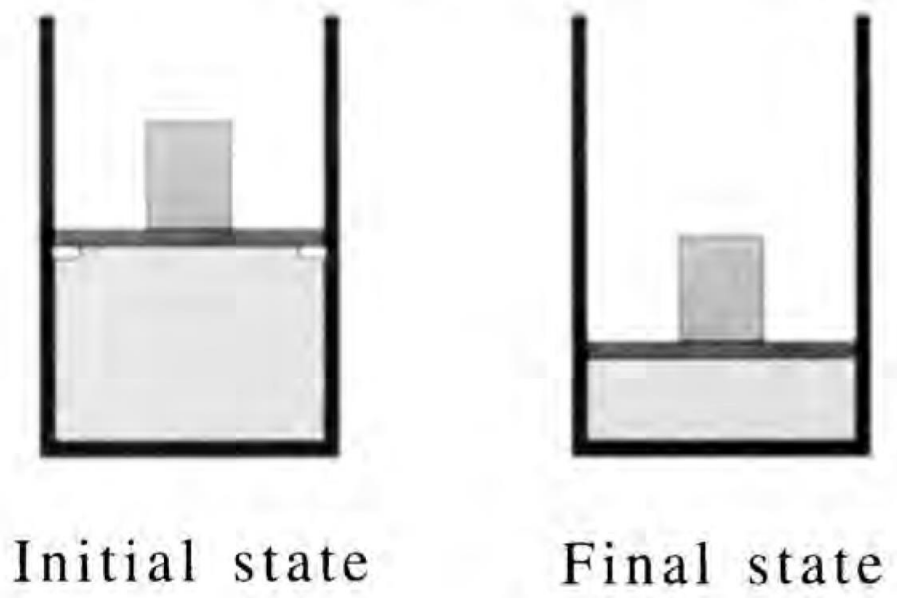


Fig. 1b: *work is done on the system because the mass is lowered.*

Pressure-Volume Work

But now $\Delta V < 0$, so $w > 0$. After the compression, we have $P_{ext} = P_f$. The work is positive because work is done *on* the gas when it is compressed.

If P_{ext} is not constant during the expansion, the work is given by

$$w = -\int_{V_i}^{V_f} P_{ext} dV \qquad (2)$$

where the limits on the integral indicate an initial state and a final state; we must have knowledge of how P_{ext} varies with V along the path connecting these two states so we can carry out the integration in Equation 2. Equation 2 is applicable to either expansion or compression. If P_{ext} is constant, Equation 2 gives Equation 1

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

EXAMPLE 1

Consider an ideal gas that occupies 1.00 dm^3 at a pressure of 2.00 bar. If the gas is compressed isothermally at a constant external pressure, P_{ext}, so that the final volume is 0.500 dm^3, what is the smallest value P_{ext} can have? Calculate the work involved using this value of P_{ext}.

SOLUTION: For a compression to occur, the value of P_{ext} must be at least as large as the final pressure of the gas. Given the inital pressure and volume, and the final volume, we can determine the final pressure. The final pressure of the gas is

$$P_f = \frac{P_i V_i}{V_f} = \frac{(2.00 \text{ bar})(1.00 \text{ dm}^3)}{0.500 \text{ dm}^3} = 4.00 \text{ bar}$$

This is the smallest value P_{ext} can be to compress the gas isothermally from 1.00 dm^3 to 0.500 dm^3. The work involved using this value of P_{ext} is

$$w = -P_{\text{ext}}\,\Delta V = -(4.00\ \text{bar})(-0.500\ \text{dm}^3) = 2.00\ \text{dm}^3 \cdot \text{bar}$$

$$= (2.00\ \text{dm}^3 \cdot \text{bar})(10^{-3}\ \text{m}^3 \cdot \text{dm}^{-3})(10^5\ \text{Pa} \cdot \text{bar}^{-1}) = 200\ \text{Pa} \cdot \text{m}^3 = 200\ \text{J}$$

Of course, P_{ext} can be any value greater than 4.00 bar, so 200 J represents the smallest value of w for the isothermal compression at constant pressure from a volume of 1.00 dm^3 to 0.500 dm^3.

Internal Energy

In thermodynamics, the total energy of a system is called its **internal energy**, U. The internal energy is the total kinetic and potential energy of the molecules in the system. We denote by ΔU the change in internal energy when a system changes from an initial state i with internal energy U_i to a final state f of internal energy U_f:

$$\Delta U = U_f - U_i \qquad [2.1]$$

Throughout thermodynamics, we use the convention that $\Delta X = X_f - X_i$, where X is a property (a 'state function') of the system.

The internal energy is a **state function** in the sense that its value depends only on the current state of the system and is independent of how that state has been prepared. In other words, internal energy is a function of the properties that determine the current state of the system. Changing any one of the state variables, such as the pressure, results in a change in internal energy.

Molecular interpretation of internal energy

A molecule has a certain number of motional degrees of freedom, such as the ability to translate (the motion of its centre of mass through space), rotate around its centre of mass, or vibrate (as its bond lengths and angles change, leaving its centre of mass unmoved). Many physical and chemical properties depend on the energy associated with each of these modes of motion. For example, a chemical bond might break if a lot of energy becomes concentrated in it, for instance as vigorous vibration.

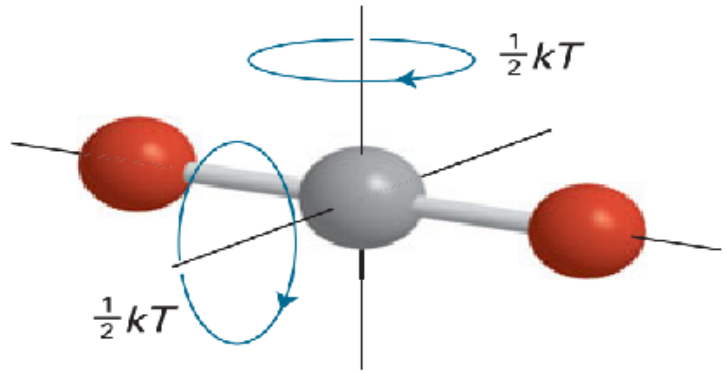
According to The 'equipartition theorem' of classical mechanics the average energy of each quadratic contribution to the energy is $\frac{1}{2}kT$.

the mean energy of the atoms free to move in three dimensions is $\frac{3}{2}kT$ and the total energy of a monatomic perfect gas is $\frac{3}{2}NkT$, or $\frac{3}{2}nRT$ (because $N = nN_A$ and $R = N_A k$). We can therefore write

$$U_m(T) = U_m(0) + \tfrac{3}{2}RT \quad \text{(monatomic gas; translation only)} \qquad (2.2a)$$

where $U_m(0)$ is the molar internal energy at $T = 0$, when all translational motion has ceased and the sole contribution to the internal energy arises from the internal structure of the atoms. This equation shows that the internal energy of a perfect gas increases linearly with temperature. At 25°C, $\frac{3}{2}RT = 3.7$ kJ mol^{-1}, so translational motion contributes about 4 kJ mol^{-1} to the molar internal energy of a gaseous sample of atoms or molecules.

When the gas consists of molecules, we need to take into account the effect of rotation and vibration. A linear molecule, such as N_2 and CO_2, can rotate around two axes perpendicular to the line of the atoms (Fig.), so it has two rotational modes of motion, each contributing a term $\frac{1}{2}kT$ to the internal energy. Therefore, the mean rotational energy is kT and the rotational contribution to the molar internal energy is RT.



By adding the translational and rotational contributions, we obtain

$$U_m(T) = U_m(0) + \tfrac{5}{2}RT \quad \text{(linear molecule; translation and rotation only)}$$

A nonlinear molecule, such as CH_4 or H_2O, can rotate around three axes and, again, each mode of motion contributes a term $\frac{1}{2}kT$ to the internal energy. Therefore, the mean rotational energy is $\frac{3}{2}kT$ and there is a rotational contribution of $\frac{3}{2}RT$ to the molar internal energy. That is,

$$U_m(T) = U_m(0) + 3RT \quad \text{(nonlinear molecule; translation and rotation only)}$$

The internal energy now increases twice as rapidly with temperature compared with the monatomic gas. Put another way: for a gas consisting of 1 mol of nonlinear molecules to undergo the same rise in temperature as 1 mol of monatomic gas, twice as much energy must be supplied. Molecules do not vibrate significantly at room temperature and, as a first approximation, the contribution of molecular vibrations to the internal energy is negligible except for very large molecules such as polymers and biological macromolecules.

None of the expressions we have derived depends on the volume occupied by the molecules: there are no intermolecular interactions in a perfect gas. That is, the internal energy of a perfect gas is independent of the volume it occupies.

Work and Heat Are Not State Functions, but Energy Is a State Function

Work and heat have a property that makes them quite different from energy. To appreciate this difference, we must first discuss what we mean by the state of a system. We say that a system is in a definite state when all the variables needed to describe the system completely are defined. For example, the state of one mole of an ideal gas can be described completely by specifying P, $\overline{V}$, and T. In fact, because P, $\overline{V}$, and T are related by $P\overline{V} = RT$, any two of these three variables will suffice to specify the state of the gas. Other systems may require more variables, but usually only a few will suffice. A *state function* is a property that depends only upon the state of the system, and not upon how the system was brought to that state, or upon the history of the system. Energy is an example of a state function. An important mathematical property of a state function is that its differential can be integrated in a normal way:

$$\int_1^2 dU = U_2 - U_1 = \Delta U$$

As the notation suggests, the value of ΔU is *independent* of the path taken between the initial and final states 1 and 2; it depends only upon the initial and final states through $\Delta U = U_2 - U_1$.

Work and heat are *not* state functions. For example, the external pressure used to compress a gas can have any value as long as it is large enough to compress the gas. Consequently, the work done on the gas,

$$w = -\int_1^2 P_{\text{ext}} dV$$

will depend upon the pressure used to compress the gas. The value of P_{ext} must exceed the pressure of the gas to compress it. The minimum work required occurs when P_{ext} is just infinitesimally greater than the pressure of the gas at every stage of the compression, which means that the gas is essentially in equilibrium during the entire compression. In this special but important case, we can replace P_{ext} by the pressure of the gas (P) When P_{ext} and P differ only infinitesimally, the process is called a *reversible process* because the process could be reversed (from compression to expansion) by decreasing the external pressure infinitesimally. Necessarily, a strictly reversible process would require an infinite time to carry out because the process must be adjusted by an infinitesimal amount at each stage.

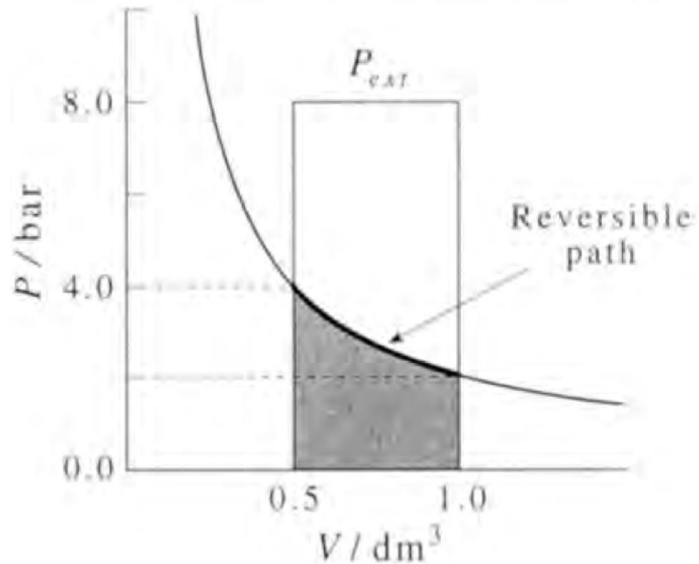
Let w_{rev} denote the reversible work for the compression of an ideal gas isothermally from V_1 to V_2,

$$w_{rev} = -\int_1^2 P_{gas}\,dV = -\int_1^2 \frac{nRT}{V}\,dV = -nRT\int_1^2 \frac{dV}{V}$$

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

P_{ext} replaced by the equilibrium value of the pressure of the gas, which is nRT/V for an ideal gas.

Because $V_2 < V_1$ for compression, we see that $w_{rev} > 0$ as it should be; in other words, we have done work on the gas.



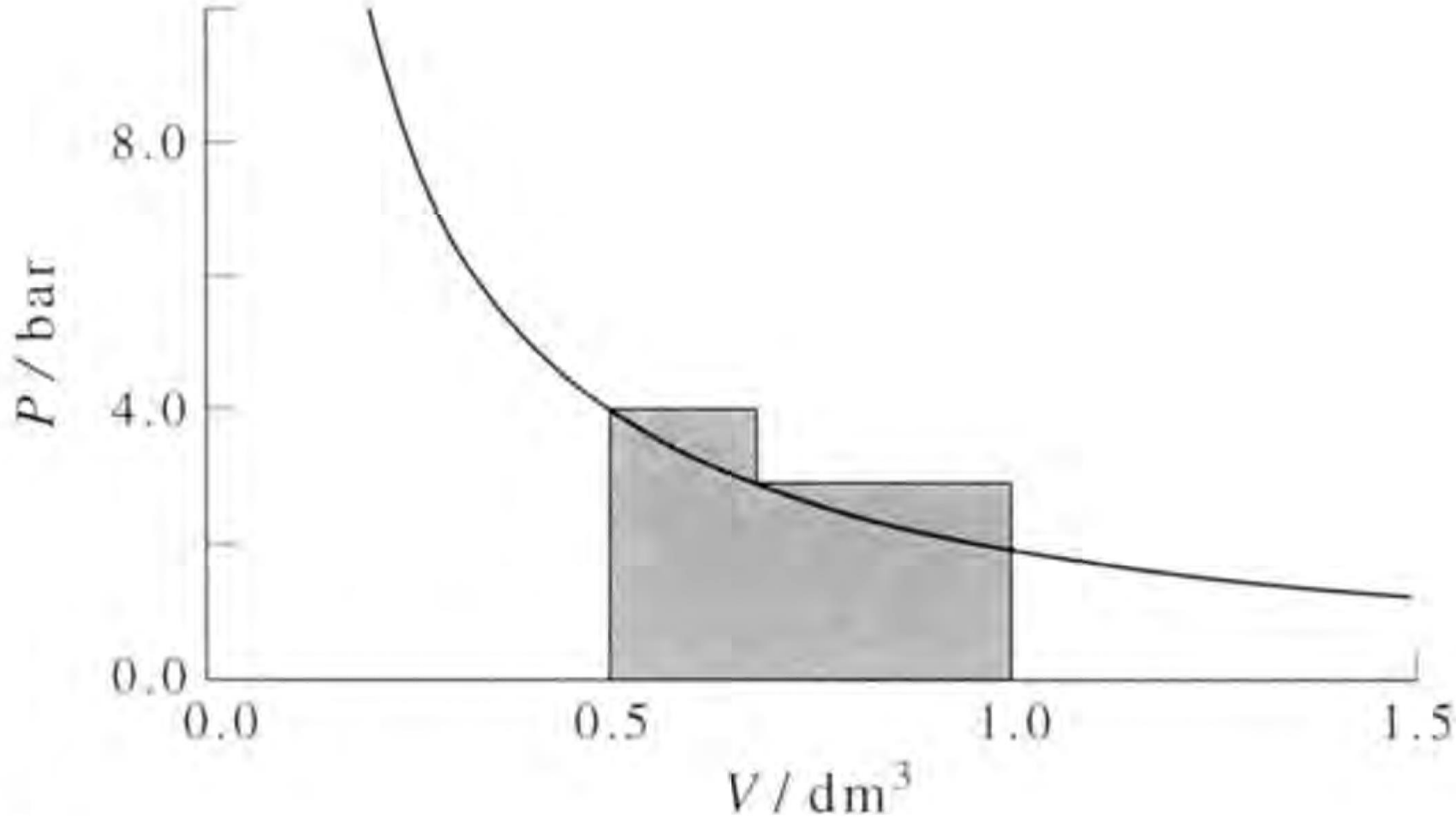
EXAMPLE

Consider an ideal gas that occupies 1.00 dm^3 at 2.00 bar. Calculate the work required to compress the gas isothermally to a volume of 0.667 dm^3 at a constant pressure of 3.00 bar followed by another isothermal compression to 0.500 dm^3 at a constant pressure of 4.00 bar (Figure 19.4). Compare the result with the work of compressing the gas isothermally and reversibly from 1.00 dm^3 to 0.500 dm^3.

SOLUTION: In the two-stage compression, $\Delta V = -(1.00 - 0.667)\ \text{dm}^3$ in the first step and $-(0.667 - 0.500)\ \text{dm}^3$ in the second step. Therefore,

$$w = -(3.00\ \text{bar})(-0.333\ \text{dm}^3) - (4.00\ \text{bar})(-0.167\ \text{dm}^3)$$

$$= 1.67\ \text{dm}^3 \cdot \text{bar} = 167\ \text{J}$$



$$w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{0.500\ \text{dm}^3}{1.00\ \text{dm}^3}$$

Because the gas is ideal and the process is isothermal, nRT is equal to either $P_1 V_1$ or $P_2 V_2$, both of which equal 2.00 $\text{dm}^3 \cdot \text{bar}$, and so

$$w_{\text{rev}} = -(2.00\ \text{dm}^3 \cdot \text{bar}) \ln 0.500 = 1.39\ \text{dm}^3 \cdot \text{bar} = 139\ \text{J}$$

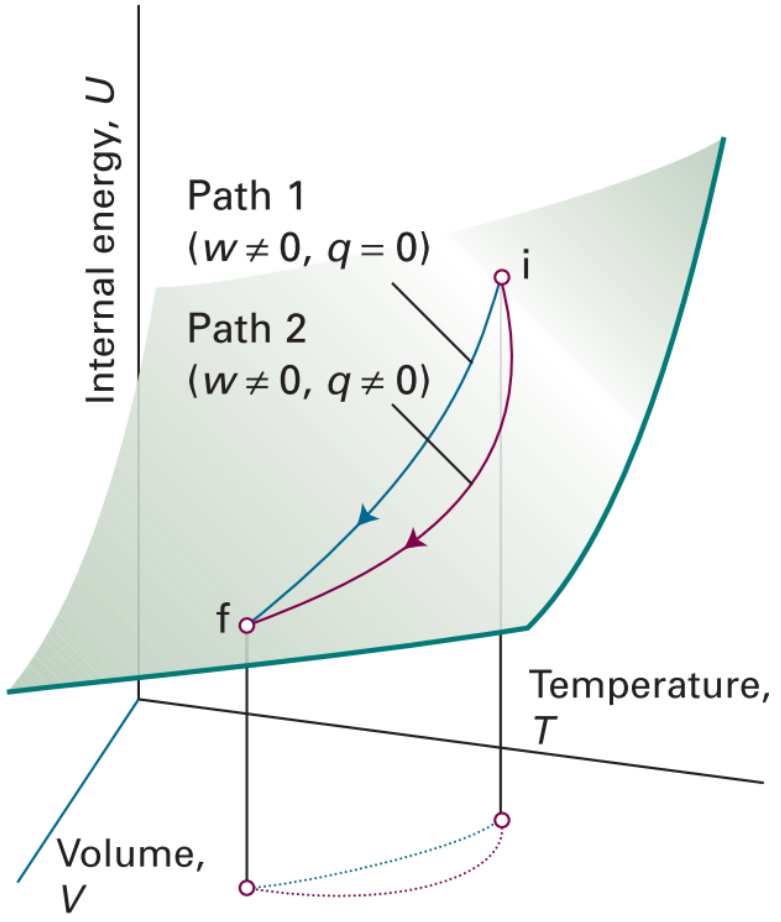
Note that w_{rev} is less than that for the two-stage process

Exact and inexact differentials

Consider a system undergoing the changes depicted in Fig. The initial state of the system is i and in this state the internal energy is U_i. Work is done by the system as it expands adiabatically to a state f. In this state the system has an internal energy U_f and the work done on the system as it changes along Path 1 from i to f is w. Notice our use of language: U is a property of the state; w is a property of the path. Now consider another process, Path 2, in which the initial and final states are the same as those in Path 1 but in which the expansion is not adiabatic. The internal energy of both the initial and the final states are the same as before (because U is a state function). However, in the second path an energy q' enters the system as heat and the work w' is not the same as w. The work and the heat are path functions.

If a system is taken along a path (for example, by heating it), U changes from U_i to U_f, and the overall change is the sum (integral) of all the infinitesimal changes along the path:

$$\Delta U = \int_i^f \mathrm{d}U$$



The value of ΔU depends on the initial and final states of the system but is independent of the path between them. This path independence of the integral is expressed by saying that dU is an 'exact differential'. In general, an **exact differential** is an infinitesimal quantity that, when integrated, gives a result that is independent of the path between the initial and final states.

When a system is heated, the total energy transferred as heat is the sum of all individual contributions at each point of the path:

$$q = \int_{\text{i, path}}^{\text{f}} \mathrm{d}q$$

Notice the differences between this equation and eqn for ΔU First, we do not write Δq, because q is not a state function and the energy supplied as heat cannot be expressed as $q_\text{f} - q_\text{i}$. Secondly, we must specify the path of integration because q depends on the path selected (for example, an adiabatic path has $q = 0$, whereas a non-adiabatic path between the same two states would have $q \neq 0$). This path-dependence is expressed by saying that dq is an 'inexact differential'. In general, an **inexact differential** is an infinitesimal quantity that, when integrated, gives a result that depends on the path between the initial and final states. Often dq is written đq to emphasize that it is inexact and requires the specification of a path.

The work done on a system to change it from one state to another depends on the path taken between the two specified states; for example, in general the work is different if the change takes place adiabatically and non-adiabatically. It follows that dw is an inexact differential. It is often written đw.

Alternatively we can say that ΔU is a state function whereas w and q are not. Mathematically, this is expressed by saying that while the differential of energy, dU, is an exact differential, the differentials of heat and work, viz., dq and dw, respectively, are inexact differentials. Exact differentials can be integrated between the appropriate limits. This cannot be done in the case of inexact differentials,

$$\int_{U_1}^{U_2} dU = U_2 - U_1$$

$$\int_{q_1}^{q_2} dq \neq q_2 - q_1 \quad \text{and} \quad \int_{w_1}^{w_2} dw \neq w_2 - w_1$$

The First Law of Thermodynamics Says the Energy Is a State Function

Because the work involved in a process depends upon how the process is carried out, work is *not* a state function. Thus, we write

$$\int_1^2 \delta w = w \qquad \text{(not } \Delta w \text{ or } w_2 - w_1\text{)} \tag{19.5}$$

It makes no sense at all to write w_2, w_1, $w_2 - w_1$, or Δw. The value of w obtained in Equation 19.5 depends upon the *path* from state 1 to 2, so work is called a *path function*. Mathematically, δw in Equation 19.5 is called an *inexact differential*, as opposed to an *exact differential* like dU, which can be integrated in the normal way to obtain $U_2 - U_1$

Work and heat are defined only for processes in which energy is transferred between a system and its surroundings. Both work and heat are path functions. Although a system in a given state has a certain amount of energy, it does not possess work or heat. The difference between energy and work and heat can be summarized by writing

$$\int_1^2 dU = U_2 - U_1 = \Delta U \qquad (U \text{ is a state function}) \qquad (19.6)$$

$$\int_1^2 \delta w = w \quad (\text{not } w_2 - w_1) \qquad (\text{path function}) \qquad (19.7)$$

$$\int_1^2 \delta q = q \quad (\text{not } q_2 - q_1) \qquad (\text{path function}) \qquad (19.8)$$

For a process in which energy is transferred both as work and heat, the law of conservation of energy says that the energy of the system obeys the equation

$$dU = \delta q + \delta w \qquad (19.9) \quad \text{in differential form}$$

$$\text{or} \quad \Delta U = q + w \qquad (19.10) \quad \text{in integrated form}$$

Equations 19.9 and 19.10 are statements of the *First Law of Thermodynamics*. The First Law of Thermodynamics, which is essentially a statement of the law of conservation of energy, also says that even though δq and δw are separately path functions or inexact differentials, their sum is a state function or an exact differential. All state functions are exact differentials.

The formulation of the First Law

It has been found experimentally that the internal energy of a system may be changed either by doing work on the system or by heating it. Whereas we may know how the energy transfer has occurred (because we can see if a weight has been raised or lowered in the surroundings, indicating transfer of energy by doing work, or if ice has melted in the surroundings, indicating transfer of energy as heat), the system is blind to the mode employed. *Heat and work are equivalent ways of changing a system's internal energy*. A system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy. It is also found experimentally that, if a system is isolated from its surroundings, then no change in internal energy takes place. This summary of observations is now known as the **First Law of thermodynamics** and is expressed as follows:

The internal energy of an isolated system is constant. — First Law of thermodynamics

We cannot use a system to do work, leave it isolated, and then come back expecting to find it restored to its original state with the same capacity for doing work. The experimental evidence for this observation is that no 'perpetual motion machine', a machine that does work without consuming fuel or using some other source of energy, has ever been built.

These remarks may be summarized as follows. If we write w for the work done on a system, q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, then it follows that

$$\Delta U = q + w \qquad (2.3)$$

Mathematical statement of the First Law

Equation 2.3 summarizes the equivalence of heat and work and the fact that the internal energy is constant in an isolated system (for which $q = 0$ and $w = 0$). The equation states that the change in internal energy of a closed system is equal to the energy that passes through its boundary as heat or work.

Enthalpy

Under constant volume conditions, no work is done on or by the system, as a result, all the heat supplied goes into raising the internal energy (U) of the system. However the change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work (see the fig.) so dU is less than dq.

At constant Volume dq = dU

At constant Pressure dq > dU = dH

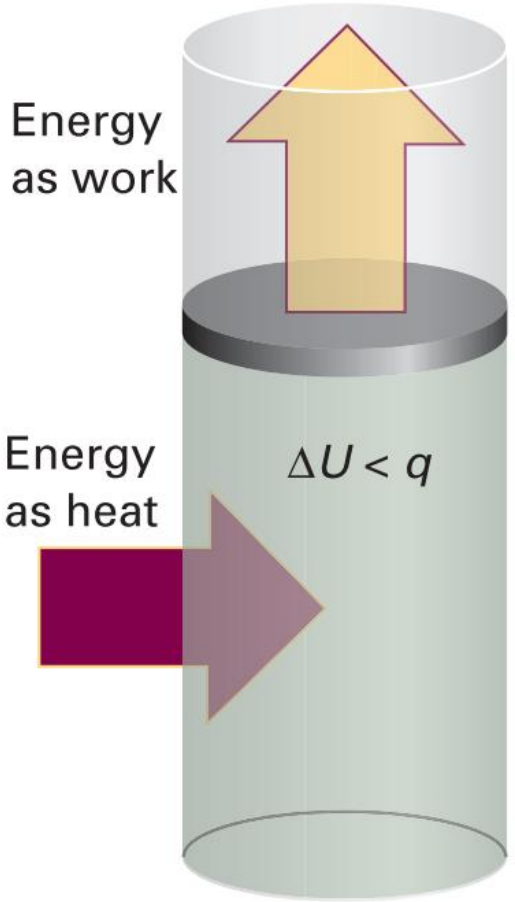


Fig. When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

The Enthalpy Change Is Equal to the Energy Transferred as Heat in a Constant-Pressure Process Involving Only $P-V$ Work

For a reversible process in which the only work involved is pressure-volume work, the first law tells us that

$$\Delta U = q + w = q - \int_{V_1}^{V_2} P dV \qquad (19.32)$$

If the process is carried out at constant volume, then $V_1 = V_2$ and

$$\Delta U = q_V \qquad (19.33)$$

where the subscript V on q emphasizes that Equation 19.33 applies to a constant-volume process. Thus, we see that ΔU can be measured experimentally by measuring the energy as heat (by means of a calorimeter) associated with a constant-volume process (in a rigid closed container).

Many processes, particularly chemical reactions, are carried out at constant pressure (open to the atmosphere). The energy as heat associated with a constant-pressure process, q_P, is not equal to ΔU. It would be convenient to have a state function analogous to U so that we could write an expression like that in Equation 19.33. To this end, let P be constant in Equation 19.32 so that

$$q_P = \Delta U + P_{\text{ext}} \int_{V_1}^{V_2} dV = \Delta U + P\Delta V \tag{19.34}$$

where we have used the subscript P on q_P to emphasize that this is a constant-pressure process. This equation suggests that we define a new state function by

$$H = U + PV \tag{19.35}$$

At constant pressure,

$$\Delta H = \Delta U + P\Delta V \qquad \text{(constant pressure)} \tag{19.36}$$

Equation 19.34 shows that

$$q_P = \Delta H \tag{19.37}$$

Thus, this new state function H, called the *enthalpy*, plays the same role in a constant-pressure process that U plays in a constant-volume process. The value of ΔH can be determined experimentally by measuring the energy as heat associated with a constant-pressure process, or conversely, q_P can be determined from ΔH. Because most chemical reactions take place at constant pressure, the enthalpy is a practical and important thermodynamic function.

Let's apply these results to the melting of ice at 0°C and one atm. For this process, $q_P = 6.01\ \text{kJ}\cdot\text{mol}^{-1}$. Using Equation 19.37, we find that

$$\Delta\overline{H} = q_P = 6.01\ \text{kJ}\cdot\text{mol}^{-1}$$

where the overbar on H signifies that $\Delta\overline{H}$ is a molar quantity. We can also calculate the value of ΔU using Equation 19.36 and the fact that the molar volume of ice ($\overline{V}_s$) is $0.0196\ \text{L}\cdot\text{mol}^{-1}$ and that of water ($\overline{V}_l$) is $0.0180\ \text{L}\cdot\text{mol}^{-1}$:

$$\Delta\overline{U} = \Delta\overline{H} - P\Delta\overline{V}$$

$$= 6.01\ \text{kJ}\cdot\text{mol}^{-1} - (1\ \text{atm})(0.0180\ \text{L}\cdot\text{mol}^{-1} - 0.0196\ \text{L}\cdot\text{mol}^{-1})$$

$$= 6.01\ \text{kJ}\cdot\text{mol}^{-1} - (1.60 \times 10^{-3}\ \text{L}\cdot\text{atm}\cdot\text{mol}^{-1})\left(\frac{8.314\ \text{J}}{0.08206\ \text{L}\cdot\text{atm}}\right)\left(\frac{1\ \text{kJ}}{10^3\ \text{J}}\right)$$

$$\approx 6.01\ \text{kJ}\cdot\text{mol}^{-1}$$

Thus, in this case, there is essentially no difference between $\Delta\overline{H}$ and $\Delta\overline{U}$.

Let's look at the vaporization of water at 100°C and one atm. For this process, $q_P = 40.7\ \text{kJ}\cdot\text{mol}^{-1}$, $\overline{V}_{\text{l}} = 0.0180\ \text{L}\cdot\text{mol}^{-1}$, and $\overline{V}_{\text{g}} = 30.6\ \text{L}\cdot\text{mol}^{-1}$. Therefore,

$$\Delta\overline{H} = q_P = 40.7\ \text{kJ}\cdot\text{mol}^{-1}$$

But $\Delta\overline{V} = 30.6\ \text{L}\cdot\text{mol}^{-1} - 0.0180\ \text{L}\cdot\text{mol}^{-1} = 30.6\ \text{L}\cdot\text{mol}^{-1}$

so $\Delta\overline{U} = \Delta\overline{H} - P\Delta\overline{V}$

$$= 40.7\ \text{kJ}\cdot\text{mol}^{-1} - (1\ \text{atm})(30.6\ \text{L}\cdot\text{mol}^{-1})\left(\frac{8.314\ \text{J}}{0.08206\ \text{L}\cdot\text{atm}}\right)$$

$$= 37.6\ \text{kJ}\cdot\text{mol}^{-1}$$

Notice that the numerical values of $\Delta\overline{H}$ and $\Delta\overline{U}$ are significantly different ($\approx 8\%$) in this case because $\Delta\overline{V}$ for this process is fairly large. We can give a physical interpretation of these results. Of the 40.7 kJ that are absorbed at constant pressure, 37.6 kJ ($q_V = \Delta\overline{U}$) are used to overcome the intermolecular forces holding the water molecules in the liquid state (hydrogen bonds) and 3.1 kJ (40.7 kJ − 37.6 kJ) are used to increase the volume of the system against the atmospheric pressure.

Assignment Problem?

The value of ΔH at 298 K and one bar for the reaction described by

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$$

is −572 kJ. Calculate ΔU for this reaction as written.

SOLUTION: Because the reaction is carried out at a constant pressure of 1.00 bar, $\Delta H = q_P = -572$ kJ. To calculate ΔU, we must first calculate ΔV. Initially, we have three moles of gas at 298 K and 1.00 bar, and so

$$V = \frac{nRT}{P} = \frac{(3\text{ mol})(0.08314\text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\text{ K})}{1.00\text{ bar}}$$
$$= 74.3\text{ L}$$

Afterward, we have two moles of liquid water, whose volume is about 36 mL, which is negligible compared with 74.3 L. Thus, $\Delta V = -74.3$ L and

$$\Delta U = \Delta H - P\Delta V$$
$$= -572\text{ kJ} + (1.00\text{ bar})(73.4\text{ L})\left(\frac{1\text{ kJ}}{10\text{ bar}\cdot\text{L}}\right) = -572\text{ kJ} + 7.43\text{ kJ}$$
$$= -565\text{ kJ}$$

The numerical difference between ΔH and ΔU in this case is about 1%.

In General $\Delta H = \Delta U + RT\Delta n_{\text{gas}}$

$$\Delta n_{\text{gas}} = \begin{pmatrix}\text{number of moles of}\\ \text{gaseous products}\end{pmatrix} - \begin{pmatrix}\text{number of moles of}\\ \text{gaseous reactants}\end{pmatrix}$$

Variation of U with Temperature: Heat Capacity at constant Volume, C_v

The internal energy of a system increases when its temperature is raised. The increase depends on the conditions under which the heating takes place and for the present we suppose that the system has a constant volume. For example, it may be a gas in a container of fixed volume. If the internal energy is plotted against temperature, then a curve like that in Fig. 2.10 may be obtained. The slope of the tangent to the curve at any temperature is called the **heat capacity** of the system at that temperature. The **heat capacity at constant volume** is denoted C_V and is defined formally as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad [2.15]$$

Definition of heat capacity at constant volume

In this case, the internal energy varies with the temperature and the volume of the sample, but we are interested only in its variation with the temperature, the volume being held constant (Fig. 2.11).

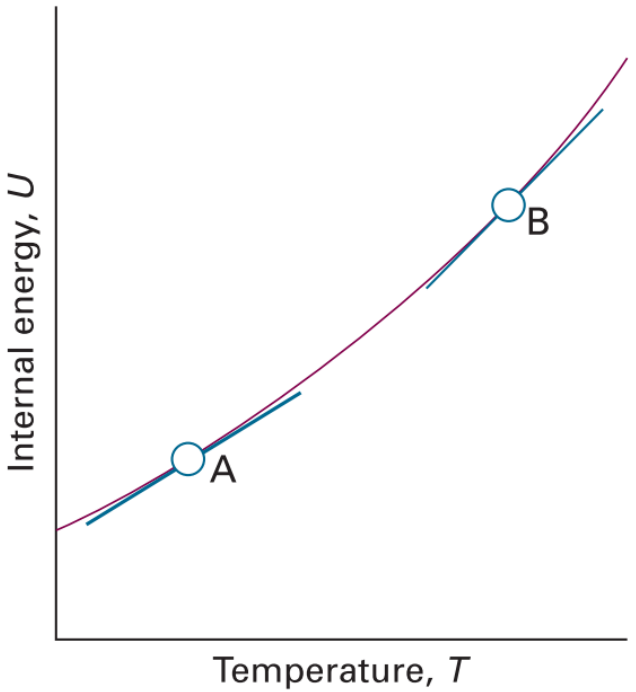


Fig. 2.10 The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A.

Variation of U with Temperature: Heat Capacity at constant Volume, C_v

The internal energy of a system increases when its temperature is raised. The increase depends on the conditions under which the heating takes place and for the present we suppose that the system has a constant volume. For example, it may be a gas in a container of fixed volume. If the internal energy is plotted against temperature, then a curve like that in Fig. 2.10 may be obtained. The slope of the tangent to the curve at any temperature is called the **heat capacity** of the system at that temperature. The **heat capacity at constant volume** is denoted C_V and is defined formally as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad [2.15]$$

Definition of heat capacity at constant volume

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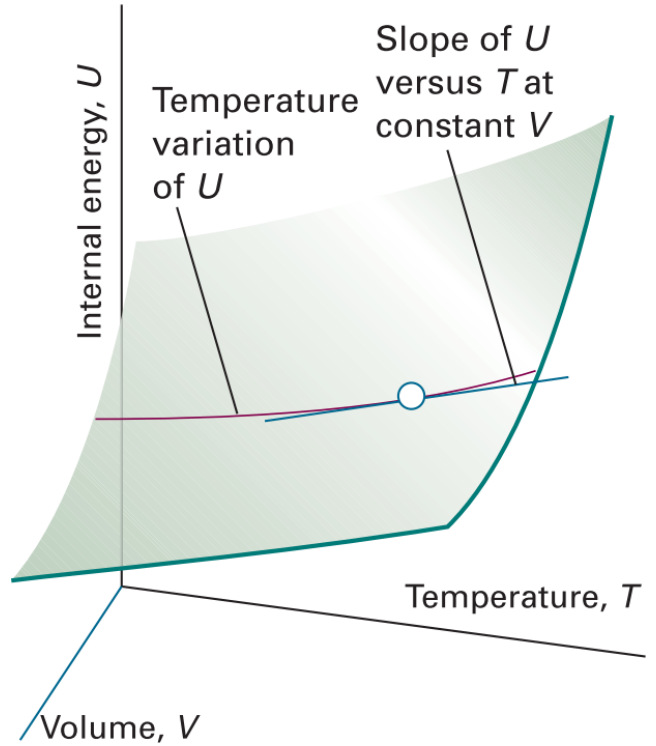

Fig. 2.11 The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface. The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to T. The slope of this curve at any point is the partial derivative $(\partial U/\partial T)_V$.

Heat capacities are extensive properties: 100 g of water, for instance, has 100 times the heat capacity of 1 g of water (and therefore requires 100 times the energy as heat to bring about the same rise in temperature). The **molar heat capacity at constant volume**, $C_{V,m} = C_V/n$, is the heat capacity per mole of substance, and is an intensive property (all molar quantities are intensive). Typical values of $C_{V,m}$ for polyatomic gases are close to 25 J K^{-1} mol^{-1}. For certain applications it is useful to know the **specific heat capacity** (more informally, the 'specific heat') of a substance, which is the heat capacity of the sample divided by the mass, usually in grams: $C_{V,s} = C_V/m$. The specific heat capacity of water at room temperature is close to 4.2 J K^{-1} g^{-1}. In general, heat capacities depend on the temperature and decrease at low temperatures. However, over small ranges of temperature at and above room temperature, the variation is quite small and for approximate calculations heat capacities can be treated as almost independent of temperature.

The heat capacity is used to relate a change in internal energy to a change in temperature of a constant-volume system. It follows from eqn 2.15 that

$$dU = C_V dT \quad \text{(at constant volume)} \tag{2.16a}$$

Variation of U with Temperature: Heat Capacity at constant Volume, C_v

That is, at constant volume, an infinitesimal change in temperature brings about an infinitesimal change in internal energy, and the constant of proportionality is C_V. If the heat capacity is independent of temperature over the range of temperatures of interest, a measurable change of temperature, ΔT, brings about a measurable increase in internal energy, ΔU, where

$$\Delta U = C_V \Delta T \quad \text{(at constant volume)} \tag{2.16b}$$

Because a change in internal energy can be identified with the heat supplied at constant volume (eqn 2.12b), the last equation can also be written

$$q_V = C_V \Delta T \tag{2.17}$$

Variation of U with Temperature: Heat Capacity at constant Volume, C_v

This relation provides a simple way of measuring the heat capacity of a sample: a measured quantity of energy is transferred as heat to the sample (electrically, for example), and the resulting increase in temperature is monitored. The ratio of the energy transferred as heat to the temperature rise it causes ($q_V/\Delta T$) is the constant-volume heat capacity of the sample.

A large heat capacity implies that, for a given quantity of energy transferred as heat, there will be only a small increase in temperature (the sample has a large capacity for heat). An infinite heat capacity implies that there will be no increase in temperature however much energy is supplied as heat. At a phase transition, such as at the boiling point of water, the temperature of a substance does not rise as energy is supplied as heat: the energy is used to drive the endothermic transition, in this case to vaporize the water, rather than to increase its temperature. Therefore, at the temperature of a phase transition, the heat capacity of a sample is infinite.

Heat Capacity of a monoatomic perfect gas at constant Volume, C_v

The heat capacity of a monatomic perfect gas can be calculated by inserting the expression for the internal energy derived

$$U_m = U_m(0) + \tfrac{3}{2}RT$$

so from eqn 2.15

$$C_{V,m} = \frac{\partial}{\partial T}(U_m(0) + \tfrac{3}{2}RT) = \tfrac{3}{2}R$$

The numerical value is 12.47 J K^{-1} mol^{-1}.

The variation of enthalpy with temperature *Heat Capacity at constant Volume, C_p*

The enthalpy of a substance increases as its temperature is raised. The relation between the increase in enthalpy and the increase in temperature depends on the conditions (for example, constant pressure or constant volume). The most important condition is constant pressure, and the slope of the tangent to a plot of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure**, C_p, at a given temperature (Fig. 2.14). More formally:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad \text{[2.22]}$$

Definition of heat capacity at constant pressure

The heat capacity at constant pressure is the analogue of the heat capacity at constant volume and is an extensive property. The **molar heat capacity at constant pressure**, $C_{p,m}$, is the heat capacity per mole of material; it is an intensive property.

The heat capacity at constant pressure is used to relate the change in enthalpy to a change in temperature. For infinitesimal changes of temperature

$$dH = C_p dT \quad \text{(at constant pressure)} \qquad (2.23a)$$

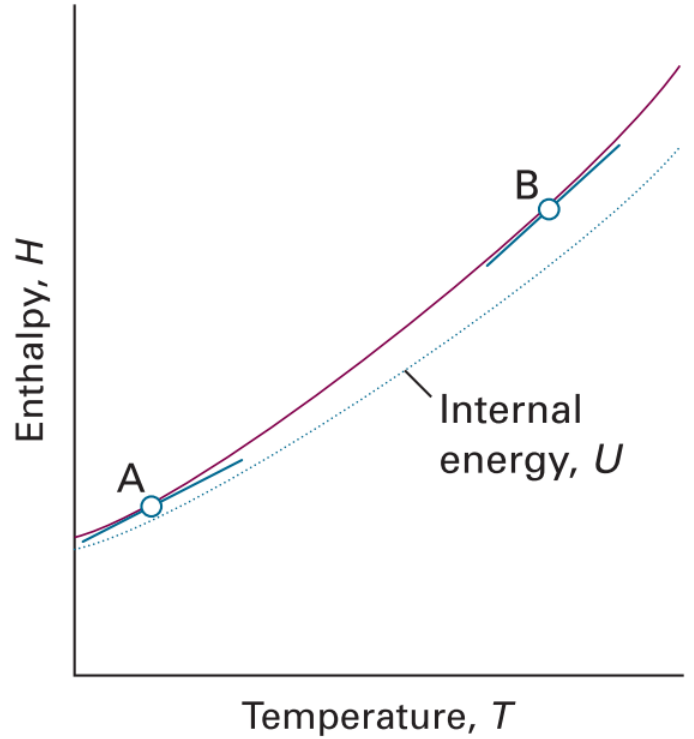

Fig. 2.14 The constant-pressure heat capacity at a particular temperature is the slope of the tangent to a curve of the enthalpy of a system plotted against temperature (at constant pressure). For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and $C_{p,m}$ is larger than $C_{V,m}$.

The variation of enthalpy with temperature *Heat Capacity at constant Volume, C_p*

If the heat capacity is constant over the range of temperatures of interest, then for a measurable increase in temperature

$$\Delta H = C_p \Delta T \quad \text{(at constant pressure)} \tag{2.23b}$$

Because an increase in enthalpy can be equated with the energy supplied as heat at constant pressure, the practical form of the latter equation is

$$q_p = C_p \Delta T \tag{2.24}$$

This expression shows us how to measure the heat capacity of a sample: a measured quantity of energy is supplied as heat under conditions of constant pressure (as in a sample exposed to the atmosphere and free to expand) and the temperature rise is monitored.

Heat Capacity Is a Path Function

- Energy as heat required to raise the temperature of a substance by **one kelvin.**
- Depends upon the **temperature T.**
- An **extensive quantity**, because the energy required to raise the temperature of a substance by one kelvin depends upon the amount of substance.
- Is a **path function** as well: its value depends upon whether we heat the substance at constant volume or at constant pressure.

At constant Volume

the added energy as heat is q_V
and the heat capacity is denoted by C_V
Because $\Delta U = q_V$, C_V is given by

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \approx \frac{\Delta U}{\Delta T} = \frac{q_V}{\Delta T}$$

At constant Pressure

the added energy as heat is q_P
heat capacity is denoted by C_P
Because $\Delta H = q_P$, C_P is given by

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \approx \frac{\Delta H}{\Delta T} = \frac{q_P}{\Delta T}$$

$$C_p > C_v$$

We expect that C_P is larger than C_V because not only do we increase the temperature when we add energy as heat in a constant-pressure process, but we also do work against atmospheric pressure as the substance expands as it is heated. Calculating the difference between C_P and C_V for an ideal gas is easy. We start with $H = U + PV$ and replace PV by nRT to obtain

$$H = U + nRT \qquad \text{(ideal gas)} \tag{19.41}$$

Notice that because U depends only upon the temperature (at constant n) for an ideal gas, H also depends only upon temperature. Thus, we can differentiate Equation 19.41 with respect to temperature to obtain

$$\frac{dH}{dT} = \frac{dU}{dT} + nR \tag{19.42}$$

But

$$\frac{dH}{dT} = \left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad \text{(ideal gas)}$$

and

$$\frac{dU}{dT} = \left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad \text{(ideal gas)}$$

so Equation 19.42 becomes

$$C_P - C_V = nR \qquad \text{(ideal gas)} \tag{19.43}$$

Joule–Thomson Effect

If the stream of a gas at high pressure is allowed to expand by passing through a porous plug into vacuum or a region of low pressure, *under adiabatic conditions*, it gets cooled appreciably. Hydrogen and helium are exceptions as they get warmed up under similar circumstances. But, at very low temperatures, these gases also show the usual behaviour. The temperature below which a gas becomes cooler on expansion is known as the **inversion temperature**. Thus, –48°C is the inversion temperature of hydrogen and –242°C is the inversion temperature of helium. The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as the **Joule–Thomson effect.** The Joule-Thomson expriment was performed in the 1850s by the two brilliant British physicists J.P. Joule (1818-1889) and William Thomson (1824-1907), later remembered as Lord Kelvin.

The cooling effect is due to decrease in the kinetic energy of the gaseous molecules since a part of this energy is used up in overcoming the van der Waals force of attraction existing between the molecules during expansion. The Joule–Thomson effect is very small when a gas approaches ideal behaviour. It has been concluded, therefore, that the Joule–Thomson effect is zero in an ideal gas. Hence, according to this view, when an ideal gas expands in vacuum, there is neither absorption nor evolution of heat, *i.e.*, $q=0$. This is quite reasonable since, in an ideal gas, the van der Waals forces are negligible and there is no expenditure of energy in overcoming these forces during expansion.

Further, when an ideal gas expands in vacuum, it does no work because the pressure against which it expands is zero. In other words, $w=0$. It follows from the general equation of the First law that $\Delta U=0$. Thus, when an ideal gas undergoes expansion under adiabatic conditions in vacuum, no change takes place in its internal energy. In other words, the internal energy of a given quantity of an ideal gas at a constant temperature is independent of its volume, *i.e.*, $(\partial U/\partial V)_T = 0$.

An ideal gas may, therefore, be defined thermodynamically by the following two equations :

(i) PV = constant, at constant temperature

(ii) $(\partial U/\partial V)_T = 0$

The quantity $(\partial U/\partial V)_T$ is called the internal pressure, as already mentioned. Thus, internal pressure of an ideal gas is zero.

Joule-Thomson Coefficient (μ_{JT}). The experimental technique used by Joule and Thomson for deriving the mathematical relation between the fall of pressure of a gas on expansion and the resulting lowering of temperature is illustrated schematically in Fig. 4.

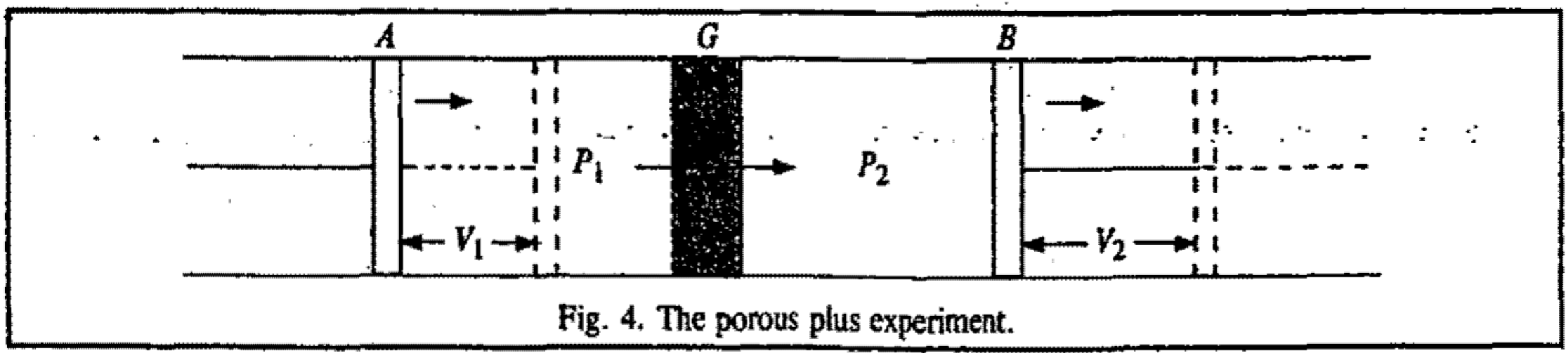

Fig. 4. The porous plus experiment.

A tube made of a non-conducting material is fitted with a porous plug G in the middle and two pistons A and B on the sides, as shown. The tube is thoroughly insulated to ensure adiabatic conditions. A volume V_1 of the gas enclosed between the piston A and the porous plug G at a pressure P_1 is forced *slowly* through the porous plug by moving the piston A inwards and is allowed to expand to a volume V_2 at a lower pressure P_2 by moving the pisten B outward, as shown.

$\therefore$ Work done on the system at the piston $A = + P_1V_1$

Work done by the system at the piston $B = - P_2V_2$

$\therefore$ Net work done by the system $= - P_2V_2 + P_1V_1$

Since the expansion of the gas has taken place adiabatically, the system is not in a position to absorb heat from the surroundings. The system, therefore, performs work at the expense of its internal energy. Consequently, the internal energy of the system changes, say, from U_1 to U_2.

$$\therefore \quad -P_2V_2 + P_1V_1 = U_2 - U_1$$

$$\text{or} \quad U_2 + P_2V_2 = U_1 + P_1V_1$$

$$\text{or} \quad H_2 = H_1 \text{ or } \Delta H = 0.$$

Thus, the Joule-Thomson expansion of a real gas occurs not with constant internal energy but with constant enthalpy. This is, therefore, called an **isenthalpic process.**

Since H is a state function, dH is a complete differential. Taking H as a function of P and T,

$$dH = (\partial H/\partial P)_T\, dP + (\partial H/\partial T)_P\, dT \qquad \ldots(76)$$

But $(\partial H/\partial T)_P = C_P$

$$\therefore \quad dH = (\partial H/\partial P)_T\, dP + C_P\, dT$$

Since for adiabatic expansion, $dH=0$, hence $(\partial H/\partial P)_T\, dP + C_P\, dT = 0$

$$\text{or} \quad \frac{dT}{dP} = -\frac{(\partial H/\partial P)_T}{C_P} \qquad \ldots(77)$$

$$i.e., \quad (\partial T/\partial P)_H = -(\partial H/\partial P)_T/C_P \qquad \ldots(78)$$

The quantity $(\partial T/\partial P)_H$ is called **Joule–Thomson coefficient** and is denoted as μ_{JT}

Assuming μ_{JT} to be constant over a small pressure range, Eq. 78 may be written as

$$\Delta T = -\frac{(\partial H/\partial P)_T}{C_P}\Delta P \qquad \ldots(79)$$

where ΔT is the fall of temperature produced as a result of the fall of pressure ΔP.

Joule and Thomson verified Eq. 79 experimentally by accurately measuring the fall of temperature (ΔT) accompanying the expansion of a number of real gases. In every case, ΔT was found to be proportional to the difference of pressure ΔP on the two sides of the porous plug, as demanded by Eq. 79.

Isothermal Expansion of an Ideal Gas: Calculation of ΔU, ΔH, w and q,

With the help of the First law pf thermodynamics it is possible to calculate changes in thermodynamic properties such as q, w, ΔU, ΔH when an ideal gas undergoes expansion. The expansion may be isothermal or adiabatic and the process of expansion may be carried out reversibly or irreversibly.

Calculation of ΔU. In an isothermal process, the temperature of the system remains constant throughout the process of expansion. Since for an ideal gas, the internal energy U depends only on temperature, it follows that at constant temperature (isothermal process), the internal energy of the gas remains constant. This means that $\Delta U = 0$.

Calculation of ΔH. $H = U + PV$

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta PV = \Delta U + \Delta nRT \qquad \ldots(23)$$

Since for an isothermal process, ΔT as well as ΔU are equal to zero, hence, $\Delta H = 0$.

Calculation of q and w. According to the First law of thermodynamics, $\Delta U = q + w$. Since, for an isothermal process, $\Delta U = 0$. hence $-w = q$. This shows that in an isothermal expansion, the work is done at the expense of the heat absorbed. The magnitude of w (or q) depends upon the manner in which the process of expansion is carried out, *i.e.*, whether it is carried out *reversibly* or *irreversibly*.

Work done in Reversible Isothermal Expansion.

$$w = -\int_{V_i}^{V_f} P_{ext} dV$$

where V_1 is the volume of the gas in the initial state *and* V_2 in the final state.

The above integral can be evaluated by substituting $P=RT/V$ for one mole of an ideal gas. Thus,

$$w = -RT\int_{V_1}^{V_2}\frac{dV}{V} = -RT\ln\frac{V_2}{V_1} \qquad ..(26)$$

Since in an ideal gas, $P_1V_1=P_2V_2$, at constant temperature, the above equation may also be written as

$$w = -RT\ln(P_1/P_2) \qquad ...(27)$$

For n moles, the above expressions may be written as

$$w = -nRT\ln(V_2/V_1) = -nRT\ln(P_1/P_2) \qquad ...(28)$$

Since during expansion, V_2 is more than V_1 and P_2 is less than P_1, hence, from Eq. 28, the work w comes out to be *negative* in conformity with the convention used in this regard.

Work done in Reversible Isothermal Compression.

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

Assuming the gas to be ideal, P, as before, may be substituted by RT/V in the above equation so that

$$w' = -RT\int_{V_2}^{V_1}\frac{dV}{V} = -RT\ln(V_1/V_2) \quad (31)$$

$$= -RT\ln(P_2/P_1) \quad (32)$$

For n moles of the gas, the above expressions may be written as

$$w' = -nRT\ln(V_1/V_2) = -nRT\ln(P_2/P_1) \quad (33)$$

Since during compression, the initial volume V_2 is more than the final volume V_1 and also since the initial pressure P_2 is less than the final pressure P_1, hence, according to Eq. 33, the work done w' comes out to be *positive*. as was chosen as a convention in this regard.

Maximum Work

It is evident from the above discussion that the magnitude of work done by a system on expansion depends upon the magnitude of the opposing (external) pressure. The closer is the opposing pressure to the pressure of the gaseous system in the cylinder, the greater is the work performed by the system on expansion. In other words maximum work is obtained when the two opposing pressures differ only by an infinitesimal amount from each other. This condition is evidently demanded for a thermodynamically reversible process. Hence, the condition for maximum work coincides with that for thermodynamic reversibility.

Work done in irreversible isothermal expansion of an ideal gas

We come across two types of irreversible isothermal expansions, viz; 1. expansion against zero pressure, i.e., in vacuum (called free expansion) and expansion against a particular constant external pressure whose magnitude is less than the P of the gas; i.e., $P_{ext} < P$ (called intermediate expansion).

Free Expansion; Since in free expansion, the external pressure is zero. therefore,

$$w = -\int dw = -\int P^{ext} dV = 0$$

Intermediate expansion; Suppose the volume of the gas increases from V1 to V2 against a constant external pressure, P_{ext}. The work done is then given by

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

Since P^{ext} is less than P, the work done during intermediate isothermal expansion is numerically less than the work done during reversible isothermal expansion in which P^{ext} is almost equal to P.

Adiabatic Expansion of an Ideal Gas: Calculation of ΔU, ΔH, w and q,

In adiabatic expansion, by definition, no heat is allowed to enter or leave the system. Hence, $q=0$. Thus, according to Eq. 2,

$$\Delta U = 0 + w \quad \text{or} \quad w = \Delta U \qquad \ldots(36)$$

In expansion, work is done *by the system* on the surroundings, hence w is negative. Accordingly, ΔU is *negative, i.e.*, there is decrease in the internal energy of the system and consequently, *the temperature of the system falls*. Evidently, the work in this case is done at the expense of the internal energy of the gas.

If there is compression, w will be positive and hence ΔU would be positive, *i.e.*, there would be increase in internal energy and consequently an increase in temperature. Evidently, in this case work is done by the surroundings on the system and this work is stored in the system in the form of an increase in internal energy.

Calculation of ΔU. As discussed earlier, the molar heat capacity at constant volume of an ideal gas is given by

$$C_V = (\partial U/\partial T)_V \qquad \ldots(37)$$

Accordingly, $dU = C_V\,dT$ and, for a finite change,

$$\Delta U = C_V \Delta T \qquad \ldots(38)$$

Adiabatic Expansion of an Ideal Gas: Calculation of ΔU, ΔH, w and q,

Calculation of ΔH. According to Eq. 9,

$$H = U + PV$$

$$\therefore \quad \Delta H = \Delta U + \Delta(PV) = \Delta U + R\Delta T \text{ for one mole of the gas,}$$

Substituting the value of ΔU from Eq. 38, we get

$$\Delta H = C_V \Delta T + R\Delta T = (C_V + R)\Delta T \qquad \ldots(39)$$

$$= C_P \Delta T \qquad \ldots(40)$$

Calculation of w. Since in an adiabatic process, $q=0$, hence according to the First law equation, $\Delta U = q + w$, the work done in this case is given by the expression

$$w = \Delta U = C_V \Delta T \qquad \ldots(41)$$

It is evident from the above equations that the magnitude of ΔU, ΔH and w would depend upon the magnitude of ΔT. Since the final temperature and hence the value of ΔT varies with the nature of the process, whether reversible or irreversible, the magnitude of the thermodynamic properties would also vary with the nature of the process.

Variation of enthalpy of a reaction with Temperature: Kirchhoff's Equation

The enthalpy of any process, whether physical or chemical, varies with temperature. The exact influence of temperature can be worked out as follows.

The enthalpy of the reaction

$$aA + bB \longrightarrow cC + dD$$

is given by $\Delta H = \Sigma H_{products} - \Sigma H_{reactants} = (cH_C + dH_D) - (aH_A + bH_B)$ ...(10)

Differentiating with respect to temperature, keeping pressure constant, we have

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = c\left(\frac{\partial H_C}{\partial T}\right)_P + d\left(\frac{\partial H_D}{\partial T}\right)_P - a\left(\frac{\partial H_A}{\partial T}\right)_P - b\left(\frac{\partial H_B}{\partial T}\right)_P$$

$$= cC_{P,C} + dC_{P,D} - aC_{P,A} - bC_{P,B} = \Delta C_P \qquad (\because C_P = (\partial H/\partial T)_P) \quad ...(11)$$

where ΔC_P = Sum of heat capacities of products – Sum of heat capacities of reactants

Eq. 11 is called the **Kirchhoff equation.** It states that *the variation of ΔH of a reaction with temperature at constant pressure is equal to ΔC_P of the system.* We can write it as

$$[\partial(\Delta H)/\partial T]_P = \Delta C_P \quad \text{or} \quad d(\Delta H) = \Delta C_P\, dT \qquad ...(12)$$

Variation of enthalpy of a reaction with Temperature: Kirchhoff's Equation

Analogously, the temperature–dependence of internal energy of reaction at constant volume is given by

$$\left[\partial(\Delta U)/\partial T\right]_v = \Delta C_v \quad \text{or} \quad d(\Delta U) = \Delta C_v\, dT \qquad \ldots(13)$$

If the temperature range of interest is small, Eqs. 12 and 13 can be easily integrated by assuming that the heat capacities are independent of temperature. Accordingly,

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_P dT = \Delta C_P \int_{T_1}^{T_2} dT \quad \text{or} \quad \Delta H_2 - \Delta H_1 = \Delta C_P(T_2 - T_1) \qquad \ldots(14)$$

$$\int_{T_1}^{T_2} d(\Delta U) = \int_{T_1}^{T_2} \Delta C_v dT = \Delta C_v \int_{T_1}^{T_2} dT \quad \text{or} \quad \Delta U_2 - \Delta U_1 = \Delta C_v(T_2 - T_1) \qquad \ldots(15)$$

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Compiled from the following books/sources

1. *Chemistry by McMurry and Fay*
2. *Physical Chemistry, Atkins, 9th Ed.*
3. *Physical Chemistry, Puri, Sharma and Pathania*
4. *Physical Chemistry, McQuirre*
5. *Internet, NPTEL etc.*