First law of Thermodynamics

Thermodynamics: Thermodynamics is the branch of physics that deals with the relationships between heat and other forms of energy in physico-chemical transformation. In particular, it describes how thermal energy is converted to and from other forms of energy and how it affects matter. Thermodynamics, then, is concerned with several properties of matter; foremost among these is heat. Heat is energy transferred between substances or systems due to a temperature difference between them.

- Thermodynamics based on three fundamental laws. These laws are not based on any theory but based on experimental facts.
- Thermodynamics can predict whether a given process will occur spontaneously or not.
- Thermodynamics deals with the state of the system and make no mention of the mechanism.
- Thermodynamics answer to why a change occurs but not how it occurs.

Thermodynamics terms

- **System:** is the part of the Universe which is chosen for thermodynamic consideration.

  The remaining portion of the universe, excluding the system, is called **surrounding.**

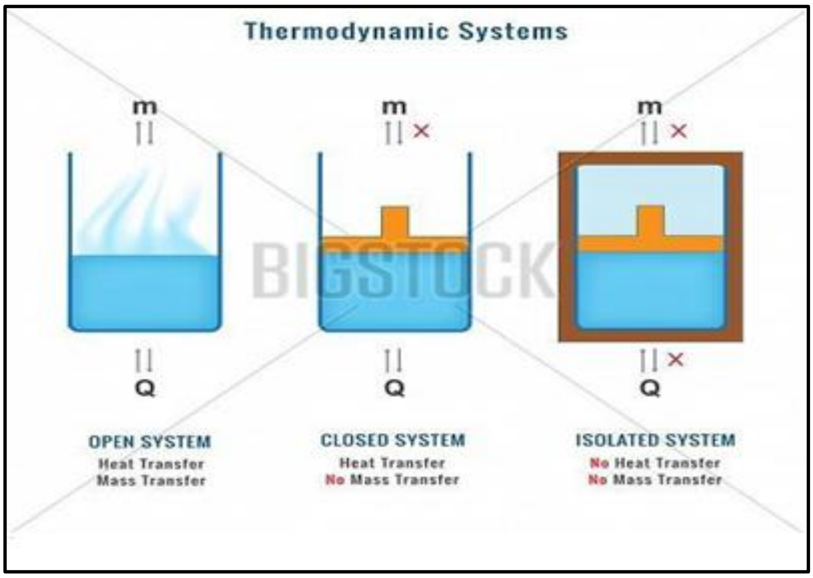
Universe = system + surrounding

A system usually consists of a definite amount of one or more substance and is separated from the surrounding by a real or imaginary boundary through which matter and energy can flow from the system to the surrounding or vice versa.

Open system: A system is said to be an open system if it can exchange both matter and energy with the surrounding.

Closed system: If a system can exchange only energy with the surrounding but not matter.

Isolated system: If a system can neither exchange matter nor energy with the surrounding**.**



Properties of a System:

- **Extensive Properties**: the quantity of matter in the system. For example, the mass of a sample is an extensive quantity; it depends on the amount of substance like mass, volume, internal energy, heat contents, free energy, entropy, and heat capacity.
- **Intensive Properties**: is a property of matter that depends only on the type of matter in a sample and not on the amount. The electrical conductivity of a substance is a property that depends only on the type of substance. Silver, gold, and copper are excellent conductors of electricity, while glass and plastic are poor conductors. Other intensive properties include color, temperature, pressure, density, surface tension, chemical potential, refractive index and solubility.

- **Process**: A thermodynamic process is defined as a change from one equilibrium state to another. The initial and final states are the defining elements of the process. ... In this process energy may be transferred form or into the system and also work can be done by or on the system.
- **Cyclic process**: It is a sequence of processes that leave the system in the same state in which it started. When a system undergoes a cyclic process, its initial and final internal energies are equal.
- **An isothermal process**: is a thermodynamic process in which the temperature of a system remains constant. The transfer of heat into or out of the system happens so slowly that thermal equilibrium is maintained.
- **An adiabatic process** is a process in which no heat is gained or lost by the system and surrounding.
- **An isochoric process**: also called a constant-volume process in which the volume of the system remains constant.
- **An isobaric process** is a process taking place at constant pressure.
- **Reversible Process:** is one which can be taken from its initial state to another state, and then back to the initial state without any change to either the system or the surroundings or during the transformation, the system does not deviate from equilibrium by more than infinitesimal amount.
- **Irreversible Process:** a process in which the system and the surroundings do not return to their original condition. This process is actual processes, carried out in finite time, occurs spontaneously and it does not remain in equilibrium during the transformation.
- **Quasi-static process:** is a thermodynamic process that happens slowly enough for the system to remain in internal thermodynamic equilibrium. An example of this is quasi-static expansion, where the volume of a system changes so slowly that the pressure remains uniform throughout the system at each instant of time during the process.

- ## Work, Heat and Energy

Energy can be exchanged between a system and its surrounding by doing work or by heating. A system does work when it cause motion against an opposing force.

Heating: is the process of transferring energy as a result of a temperature difference between the system and its surrounding. So we can define Heat is the energy transferred between two objects (or two parts of a system) because of a temperature difference.

Work is motion against an opposing force. Doing work is equivalent to raising a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston and raises a weight.

Mechanical work is defined as an energy transfer to the system through the change of an external parameter. Work is the only energy which is transferred to the system through external forces.

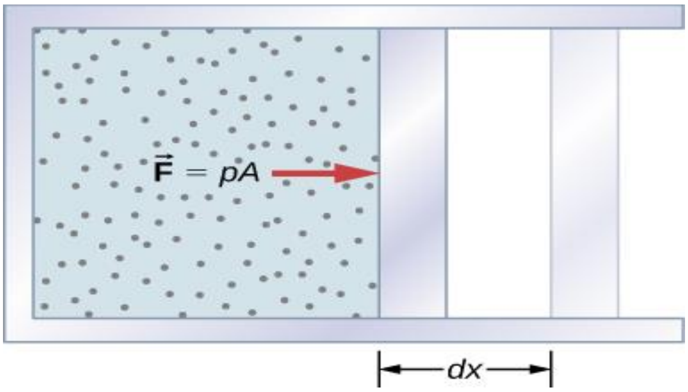


Figure (6) Work Done by a System

A force created from any source can do work by moving an object through a displacement. Then how does a thermodynamic system do work? (Figure 6) shows a gas confined to a cylinder that has a movable piston at one end. If the gas expands against the piston, it exerts a force through a distance and does work on the piston. If the piston compresses the gas as it is moved inward, work is also done - in this case, on the gas. The work associated with such volume changes can be determined as follows: Let the gas pressure on the piston face be **p**. Then the force on the piston due to the gas is **pA**, where **A** is the area of the face. When the piston is pushed outward an infinitesimal distance **dx**, the magnitude of the work done by the gas is

$$dW = Fdx = pAdx$$

Since the change in volume of the gas is dV= Adx , this becomes

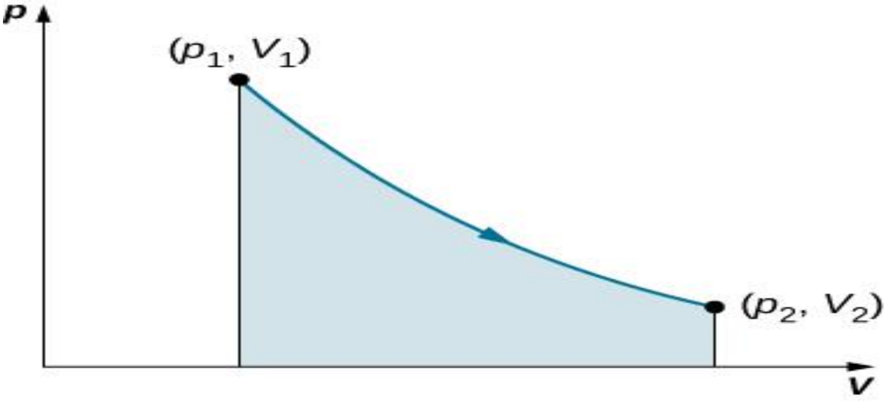
$$dW = PdV$$

For a finite change in volume from V_1 to V_2 we can integrate this equation from V_1 to V_2 to find the net work:

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

This integral is only meaningful for a quasi-static process, which means a process that takes place in infinitesimally small steps, keeping the system at thermal equilibrium. Only then does a well-defined mathematical relationship (the equation of state) exist between the pressure and volume. This relationship can be plotted on a **pV** diagram of pressure versus volume, where the curve is the change of state. We can approximate such a process as one that occurs slowly, through a series of equilibrium states. The integral is interpreted graphically as the area under the **PV** curve (the shaded area of (Figure7). Work done by the gas is positive for expansion and negative for compression.

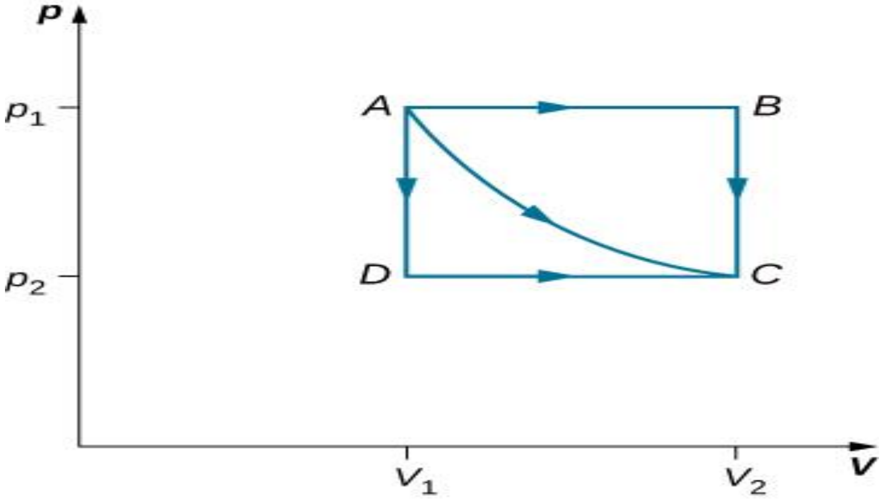
When a gas expands slowly from V_1 to V_2 the work done by the system is represented by the shaded area under the **PV** curve.



(Figure 7): **PV** curve

Consider the two processes involving an ideal gas that are represented by paths **AC** and **ABC** in (Figure 8). The first process is an isothermal expansion, with the volume of the gas changing its volume from V_1 to V_2. This isothermal process is represented by the curve between points **A** and **C**. The gas is kept at a constant temperature **T** by keeping it in thermal equilibrium with a heat reservoir at that temperature. From (Figure 8) and the ideal gas law,

$$W = \int_{V_1}^{V_2} P dV = W = \int_{V_1}^{V_2} \left(\frac{nRT}{V}\right) dV$$



(Figure 8): work done in thermodynamic process

The expansion is isothermal, so *T* remains constant over the entire process. Since *n* and *R* are also constant, the only variable in the integrand is *V*, so the work done by an ideal gas in an isothermal process is:

$$W = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}$$

Notice that if $V_2 > V_1$ (expansion), *W* is positive, as expected.

The straight lines from *A* to *B* and then from *B* to *C* represent a different process. Here, a gas at a pressure P_1first expands isobarically (constant pressure) and quasi-statically from V_1 to V_2, after which it cools quasi-statically at the constant volume V_2 until its pressure drops to P_1. From *A* to *B*, the pressure is constant at *p*, so the work over this part of the path is:

$$W = \int_{V_1}^{V_2} PdV = P_1 \int_{V_1}^{V_2} dV = P_1 (V_2 - V_1)$$

From *B* to *C*, there is no change in volume (dV=0) and therefore no work is done

$$W = \int_{V_1}^{V_2} PdV = 0$$

The net work over the path *ABC* is then:

$$W = P_1 (V_2 - V_1) + 0 = P_1 (V_2 - V_1)$$

A comparison of the expressions for the work done by the gas in the two processes of (Figure 8) shows that they are quite different. This illustrates a very important property of thermodynamic work: It is **path dependent**. We cannot determine the work done by a system as it goes from one equilibrium state to another unless we know its thermodynamic path. Different values of the work are associated with different paths.

Check Your Understanding How much work is done by the gas, as given in (Figure), when it expands quasi-statically along the path **ADC**?

State function a physical quantity is said to be state function if its value depends only upon the state of the system and does not depend upon the path by which this state has been attained. For examples: pressure, volume, temperature.

Energy, enthalpy, internal and entropy are state quantities because they describe quantitatively an equilibrium state of a thermodynamic system, irrespective of how the system arrived in that state.

Path functions are properties or quantities whose values depend on the transition of a system from the initial state to the final state. The two most common path functions are heat and work.

Work in Reversible expansion of a gas

$$W_{rev} = -\int_{V_1}^{V_2} P_{ext}\, dV$$

For expansion of the gas, Pext should be less than the pressure (P) of the gas

$$P_{ext} = P - dP.\ dP \text{ is small} \rightarrow P_{ext} = P$$

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

If gas behaves ideally:

$$-W = \int_{V_1}^{V_2} \left(\frac{nRT}{V}\right) dV = nRT \ln\frac{V_2}{V_1} = nRT \ln\frac{P_1}{P_2} \leftarrow \textit{isothermal reversible}$$

Work in Irreversible expansion of a gas

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

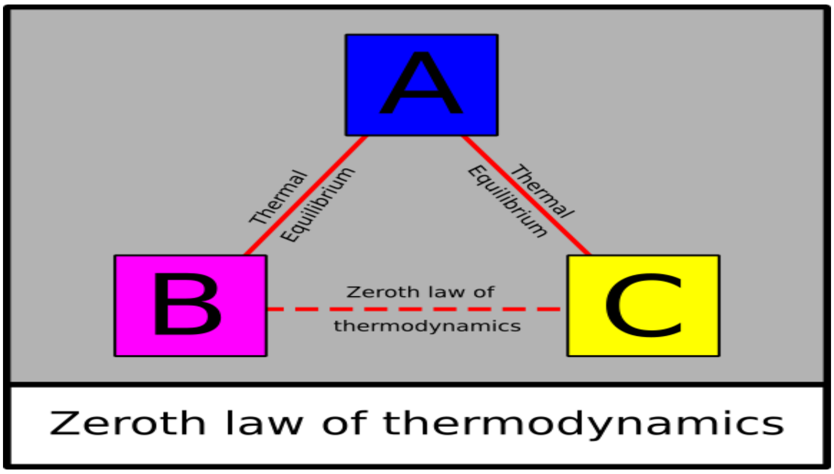
Expansion against constant pressure is irreversible expansion.

NOTE:

- When the system does work and loses energy (w is negative).
- In the Expansion $V_2 > V_1 \rightarrow$ **W= +**
- In the Compression $V_2 < V_1 \rightarrow$ **W= -**
- When the energy increased work has become done on the system (W is positive).
- When the External pressure is zero (W=0). Expansion against zero external pressure is called free expansion. (or called gas expands in vacuum).

Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states that if two bodies are each in thermal equilibrium with some third body, then they are also in equilibrium with each other. ... This basically explains that if objects A and B are each in thermal equilibrium with object C, then A and B are in thermal equilibrium with each other. Thermal equilibrium means that when two bodies are brought into contact with each other and separated by a barrier that is permeable to heat, there will be no transfer of heat from one to the other.



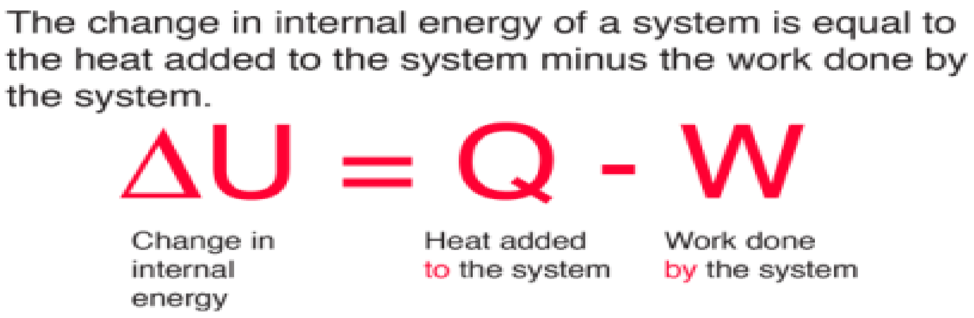
First Law of Thermodynamics

The first law of thermodynamics is a version of the law of conservation of energy (Energy cannot be created or destructed but may be transformed from one form to another).

This is mean:

- Whenever a quantity of one kind of energy is produced, an exactly equivalent of other kinds must disappear.
- The total energy of a system and its surrounding must remain constant, although it may be changed from one form to another.

The first law of thermodynamics defines the internal energy (ΔU) as equal to the difference of the heat transfer (q) **into** a system and the work (W) done **by** the system.



The change in internal energy of a system is equal to the heat added to the system minus the work done by the system.

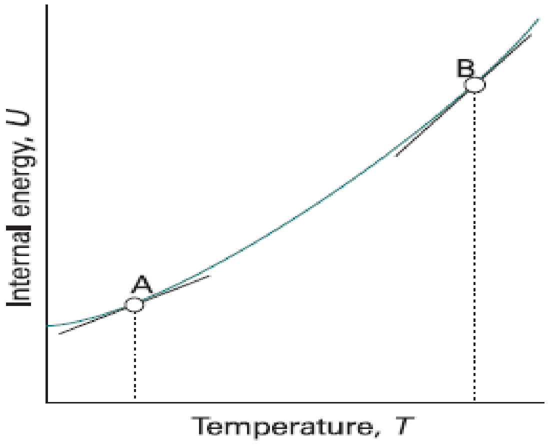
$$\Delta U = Q - W$$

This is a particularly important law when discussing heat engines (like car engines), because it helps to understand that heat must go somewhere—the basis for cogeneration. As an engine creates heat, if the heat is not vented, the engine will become hotter and hotter, which will eventually lead to melting. Therefore, because it is impossible to achieve 100% efficiency , heat must be vented. This can either be treated as waste heat, or used for cogeneration, which is applying the waste heat to another cause, like heating a car, or heating houses.

Heat Capacity:

The internal energy of a substance 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 sample is confined to a constant volume. For example, the sample 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 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:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$



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**, $C_{V,\mathrm{m}} = C_V/n$, is the heat capacity per mole of material, and is an intensive property (all molar quantities are intensive). Typical values of $C_{V,\mathrm{m}}$ 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 or is defined by the amount of heat needed to raise the temperature of 1 gram of a substance 1 degree Celsius, usually in grams: $C_{V,s} = C_V/m$. The specific heat capacity of water at room temperature is close to 4 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:

$$dU = C_V dT \quad at\ constant\ volume$$

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

$$\Delta U = C_V \Delta T \quad at\ constant\ volume$$

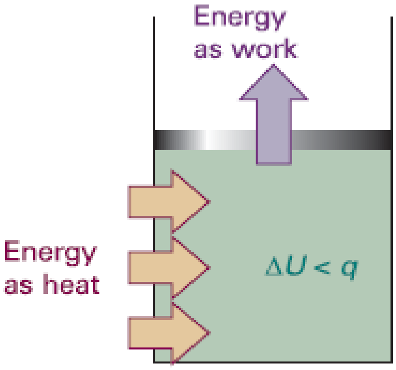
Because a change in internal energy can be identified with the heat supplied at constant Volume, the last equation can be written:

$$q_V = C_V \Delta T$$

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 raise it causes ($q_V/\Delta T$) is the constant-volume heat capacity of the sample.

Heat Content or Enthalpy

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. So dU is less than dq. However, we shall now show that 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.



The **enthalpy**, H, is defined as:

$$H = U + PV$$

Where P is the pressure of the system and V is its volume. Because U, p, and V are all state functions, the enthalpy is a state function too. As is true of any state function, the change in enthalpy, ΔH, between any pair of initial and final states is independent of the path between them.

When a process is carried out at constant volume, no mechanical work is done:

$$V = constant \rightarrow \Delta V = 0$$

$$W = P\Delta V \rightarrow W = 0$$

$$\Delta U = q - W \rightarrow \ \Delta U = q$$

If the process is carried out at constant pressure:

$$\Delta U = U_2 - U_1 = q_P - W = q_P - P(V_2 - V_1)$$

$$U_2 - U_1 = q_P - P(V_2 - V_1)$$

$$q_P = (U_2 - U_1) + P(V_2 - V_1)$$

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

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

$$as\ \Delta P = 0 \rightarrow q_P = U + P\Delta V$$

$$q_P\ is\ the\ Enthalpy = H$$

$$H = q_P\ \ (at\ constant\ pressure\ the\ enthalpy\ is\ equal\ heat)$$

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

The enthalpy of a perfect gas is related to its internal energy by using $pV = nRT$ in the definition of H:

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

This relation implies that the change of enthalpy in a reaction that produces or consumes gas is:

$$\Delta H = U + \Delta nRT$$

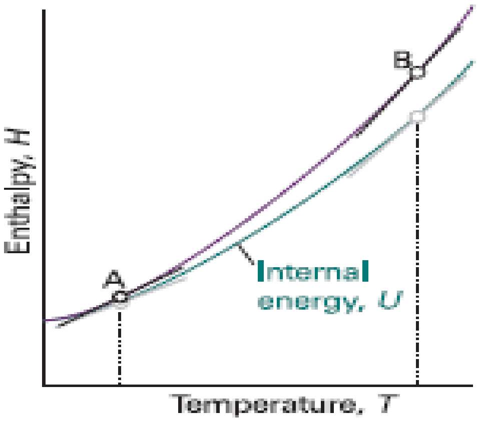
Where Δn is the change in the amount of gas molecules in the reaction

.

The variation of enthalpy with temperature

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. More formally:

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



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**, $C_{p,\mathrm{m}}$, 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:

$$dH = C_P dT \quad at\ constant\ pressure$$

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

$$\Delta H = C_P \Delta T \quad at\ constant\ pressure$$

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

$$q_P = C_P \Delta T$$

Relation between C_P and C_V

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \ldots\ldots\ldots(\mathbf{1})$$

As H= U+ PΔV

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

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \ldots\ldots.(2)$$

$$\boldsymbol{U = f(T,V)}$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \ldots\ldots(3)$$

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

Divided the equation on dT at constant pressure:

$$\left(\frac{dU}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{\partial T}\right)_P \ldots\ldots(4)$$

Substitute eq. 4 in eq. 2

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P - C_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$

$$\left(\frac{\partial U}{\partial V}\right)_T \textit{ is very small in gas and equal zero for ideal gas}$$

$$C_P - C_V = \boldsymbol{P}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\textit{for one mole of ideal gas} \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$C_P - C_V = \boldsymbol{P} \times \frac{R}{P} = R$$

$$\boldsymbol{C_P - C_V = R}$$

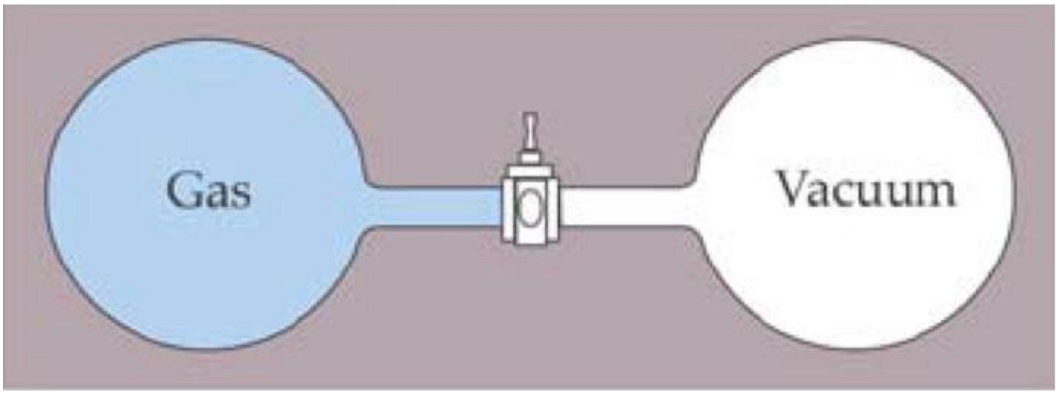
Joule's Experiment

For a closed system, the state function U is determined by T and V alone

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

Joule tried to measure this partial derivative $\left(\frac{\partial U}{\partial V}\right)_T$

In this experiment, Joule introduced a gas in a container linked to another one where a vacuum had been made. The complete system is isolated from the outside world so that it cannot exchange any type of energy in the form of heat. A valve that is initially closed separates both containers. When the valve is opened the gas expands freely towards the container where the vacuum is made until it fills the complete volume of the two containers and allowed to attain equilibrium and the temperature of the bath is recorded. Joule observed no change in temperature of thermostat. If we wait until the gas completely returns to the initial container while the other ones is completely empty, we will probably lose our time and will get old because the process is irreversible.



The thermodynamic implications of the experiment are as follows. No work was done in the expansion into a vacuum, so $w = 0$. No energy entered or left the system (the gas) as heat because the temperature of the bath did not change, so $q = 0$. Consequently, within the accuracy of the experiment, $\Delta U = 0$. It follows that U does not change much when a gas expands isothermally:

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

For ideal gas when T constant and V changes

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

For ideal gas when T constant and P changes

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

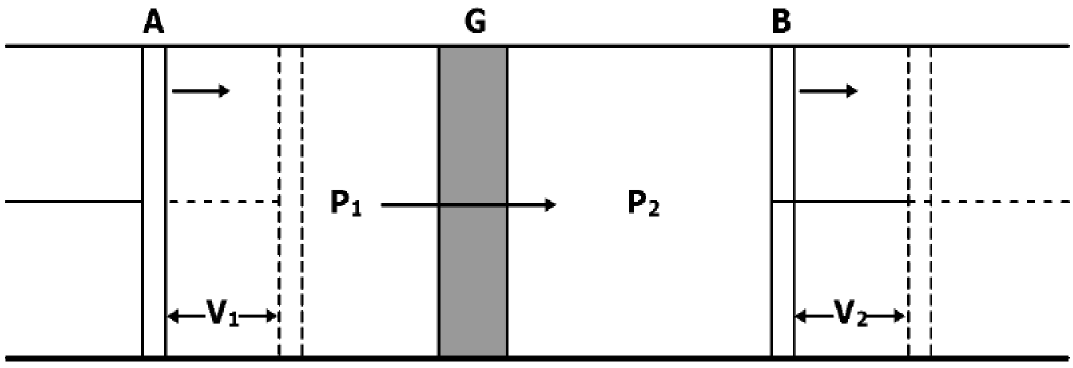
Joule – Thomson effect

Joule-Thomson effect can be defined as the phenomenon of temperature change produced when a gas is allowed to expand adiabatically from a region of high pressure to a region of extremely low pressure. This cooling of the gas is basically due to the decrease in the kinetic energy of the gaseous molecules as some part of this kinetic energy is utilized in overcoming intermolecular van der Waals force of attraction during expansion. The Joule-Thomson effect is very small when a gas approaches ideal behavior. Thus for an ideal gas, Joule Thomson effect is zero. Therefore, no absorption or evolution of heat takes place when expansion of an ideal gas occurs i.e. q = 0.This is because in an ideal gas there are no intermolecular van der Waals forces of attraction thus there is no expenditure of energy in overcoming these forces during expansion. Further, when expansion of ideal gas occurs in vacuum then no work is done since pressure against which it expands is zero. From the first law equation we can say that ΔU is also equal to zero. 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.

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

Joule Thomson Coefficient ($\mu_{J.T.}$)

Joule and Thomson derived the relationship between fall of pressure of gas on expansion and resulting lowering of temperature by performing the following technique:



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. Let the volume of gas enclosed between the piston A and the porous plug G at pressure P_1 is V_1. This volume is forced to pass through porous plug by moving the piston A inwards. At the same time the volume of gas enclosed between porous plug G and piston B i.e. V_2 is allowed to expand at a lower pressure P_2 by moving the piston B outward, as shown.

Therefore, work done on the system at the piston A = $+P_1V_1$ and work done by the system at the piston B = $-P_2V_2$.

Since the expansion of the gas is done adiabatically i.e. no exchange of heat takes place between the system and surroundings. Thus the work is done by the system at the expense of internal energy only. Let the internal energy of the system changes from U_1 to U_2.

$$-P_2V_2 = P_1V_1 = U_2 - U_1$$

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1$$

This states that the Joule-Thomson expansion of a real gas occurs with constant enthalpy and not with constant internal energy. According to this the process is known as **isoenthalpic process**.

Taking enthalpy as the function of temperature and pressure, then the total differential of the enthalpy H can be written as:

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$\text{But } \left(\frac{\partial H}{\partial T}\right)_P = C_P$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT$$

Since for adiabatic expansion, dH = 0, hence

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT = 0$$

Rearranging the above equation

$$\left(\frac{dT}{dP}\right)_H = \frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_P} \dots\dots\dots (6)$$

The quantity $\left(\frac{dT}{dP}\right)_H$ is called Joule-Thomson coefficient and it is denoted as **(μJ.T.)** .

Joule-Thomson Coefficient for an Ideal Gas.

Since H = U + PV, substituting this in equation 6 we get:

$$\left(\frac{dT}{dP}\right)_H = \mu_{J.t} = -\frac{[\partial(U + PV)/\partial P)T]}{C_P}$$

$$= -\frac{\left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial PV}{\partial P}\right)_T}{C_P}$$

$$= -\frac{\left(\frac{\partial U}{\partial P} \times \frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial PV}{\partial P}\right)_T}{C_P}$$

As the internal energy of an ideal gas at constant temperature is independent of its volume i.e. for an ideal gas, $(\Delta U / \Delta V)_T$ is zero, therefore

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

Also, PV is independent of temperature in the case of ideal gas $\left(\frac{\partial PV}{\partial P}\right)_T = 0$

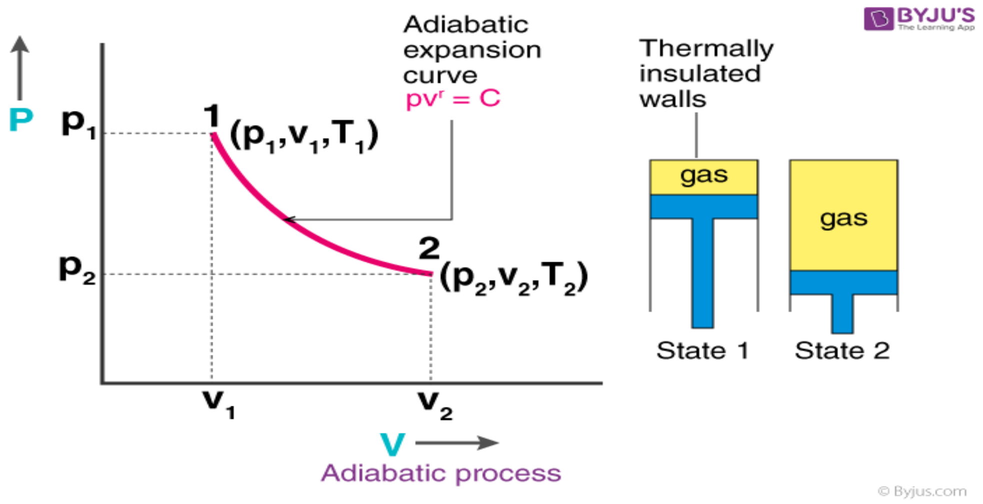
Hence $\mu_{J.t} = 0 \; for \; ideal \; gas$

Adiabatic change in state

The thermodynamic process in which there is no exchange of heat from the system to its surrounding neither during expansion nor during compression.

The adiabatic process can be either ***reversible or irreversible.*** Following are the essential conditions for the adiabatic process to take place:

- The system must be perfectly insulated from the surrounding.
- The process must be carried out quickly so that there is a sufficient amount of time for heat transfer to take place.



Reversible Adiabatic Process

Reversible adiabatic process is also called an Isentropic Process. It is an idealized thermodynamic process that is adiabatic and in which the work transfers of the system are frictionless; there is no transfer of heat or of matter and the process is reversible. Such an idealized process is useful in engineering as a model of and basis of comparison for real processes.

In adiabatic process $\partial q = 0 \rightarrow \Delta U = w$

$$\int_{U_1}^{U_2} dU = nC_V\, dT = -PdV \qquad , dT = T_2 - T_1$$

For one mole of ideal gas, $T = \frac{PV}{R}$

$$\Delta U = C_V\left(\frac{P_2V_2}{R} - \frac{P_1V_1}{R}\right)$$

$$\Delta U = \frac{C_V}{R}(P_2V_2 - P_1V_1)$$

$$R = C_P - C_V$$

$$\Delta U = C_V\frac{(P_2V_2 - P_1V_1)}{(C_P - C_V)}$$

Divided on C_V

$$\Delta U = \frac{(P_2V_2 - P_1V_1)}{\frac{(C_P - C_V)}{C_V}}$$

$$U = \frac{(P_2V_2 - P_1V_1)}{\frac{C_P}{C_V} - 1} \qquad , \frac{C_P}{C_V} = \gamma$$

$$U = \frac{(P_2V_2 - P_1V_1)}{\gamma - 1}$$

Relation between temperature and volume in reversible adiabatic changes

$$\Delta U = C_V dT = -PdV \qquad , for\ one\ mole\ of\ ideal\ gas\ P = \frac{RT}{V}$$

$$C_V dT = -\frac{RT}{V}\, dV$$

$$C_V \frac{dT}{T} = -R\frac{dV}{V}$$

If C_v is assumed to be temperature independent, then it is possible to integrate the above equation within specified limit. The result is

$$\boldsymbol{C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R\int_{V_1}^{V_2} \frac{dV}{V}}$$

$$\boldsymbol{C_V \ln\frac{T_2}{T_1} = -R\ ln\ \frac{V_2}{V_1}}$$

$$\boldsymbol{C_V \ln\frac{T_2}{T_1} = R\ ln\ \frac{V_1}{V_2}}$$

$$\ln\frac{T_2}{T_1} = \frac{R}{C_V}\ ln\ \frac{V_1}{V_2}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_P - C_V}{C_V}}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$(TV)^{\boldsymbol{\gamma-1}} = constant$$

Relation between volume and pressure in reversible adiabatic changes

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{T_2}{T_1}=\frac{P_2V_2}{P_1V_1}$$

Substitute the following value in the above equation:

$$\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\frac{P_2V_2}{P_1V_1}=\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\frac{P_2}{P_1}=\left(\frac{V_1}{V_2}\right)^{\left(\frac{R}{C_V}\right)-1}$$

$$\frac{P_2}{P_1}=\left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$\boldsymbol{PV^{\gamma}=constant}$$

Relation between temperature and pressure in reversible adiabatic changes

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$$

$$\frac{V_1}{V_2}=\frac{P_2T_1}{P_1T_2}$$

Substitute in:

$$\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\frac{T_2}{T_1}=\left(\frac{P_2T_1}{P_1T_2}\right)^{\frac{R}{C_V}}$$

$$\frac{T_2}{T_1}=\left(\frac{P_2T_1}{P_1T_2}\right)^{\gamma-1}$$

$$\left(\frac{T_2}{T_1}\right)\left(\frac{T_2}{T_1}\right)^{\gamma-1}=\left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$\left(\frac{T_2}{T_1}\right)\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$\left(\frac{T_2}{T_1}\right)\left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}}$$

$$\frac{T_2}{(P_2)^{\frac{R}{C_P}}} = \frac{T_1}{(P_1)^{\frac{R}{C_P}}} = constant$$

We can summarize the results as

$$\frac{1}{R}\ln\frac{T_2}{T_1} = \frac{1}{C_V}\ln\frac{V_1}{V_2} = \frac{1}{C_P}\ln\frac{P_2}{P_1}$$

Adiabatic Irreversible Changes

$$-W_{irr} = P_{ext}\,\Delta V$$

$$if\ P_{ext} = P_2 \qquad , \quad -W_{irr} = P_2\,(V_2 - V_1)$$

$$\Delta U = W_{irr} = -P_2\,(V_2 - V_1) = \mathrm{n}C_V\,(T_2 - T_1)$$

$$V_2 = \frac{nRT_2}{P_2} \qquad , \qquad V_1 = \frac{nRT_1}{P_1}$$

$$\Delta U = W_{irr} = -P_2\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right) = \mathrm{n}C_V\,(T_2 - T_1)$$

Adiabatic free expansion

$$W = 0 \qquad , \qquad q = 0$$

$$\Delta U = W_{irr} = \mathrm{n}C_V\,(T_2 - T_1) = 0$$

$$\Delta H = \mathrm{n}C_P\,(T_2 - T_1) = 0, \quad T_2 = T_1$$

Solved Exercises

Example 1: Two mole of nitrogen gas at 25 C was expanded reversibly and isothermally from 10 L to 20 L. calculate the work done.

$$W_{rev} = -nRT\, ln\frac{V_2}{V_1}$$

$$W_{rev} = -2.303nRT\, log\frac{V_2}{V_1}$$

$$= -2.303 \times 2 \times 8.314 \times 298\, log\, \frac{20}{10}$$

$$= 3435.2\, J$$

Example 2: One mole of oxygen at 300 K expands isothermally from 3 atm to 1 atm. Assuming that oxygen behaves ideally, calculate W: 1) if the expansion is reversible 2) if the expansion against constant pressure of 1 atm.

Solution: the initial volume of the gas V_1 is given by:

$$V_1 = \frac{nRT}{P} = \frac{1\, mol\, \times (0.08021) \times 300}{3\, atm} = 8.21\, L$$

$$V_2 = \frac{nRT}{P} = \frac{1\, mol\, \times (0.08021) \times 300}{1\, atm} = 24.63\, L$$

For process (1)

$$-W_{rev} = nRT\, ln\frac{P_1}{P_2} = 1\, mol\, \times (8.314) \times 300\, \times 2.303 \log\frac{3}{1} = 2.74\, J$$

For process (2) $-W_{rev} = P\Delta V = P_2\,(V_2 - V_1)$

$$= 1 \times 101325\, N.m^{-2}(24.63 - 8.21) \times 10^{-3} m^3 = 16.637\, kJ/mol$$

Example3: An ideal gas was expanded reversibly and isothermally from V_1 to 10 V_1 when 10000 cal of work was achieved, if the initial pressure was 100 atm. Calculate V_1.

$$-W_{rev} = nRT\, ln\frac{V_2}{V_1} = nRT \ln\frac{10V_1}{V_1}$$

$$10000 = nRT \ln 10$$

$$\frac{10000}{2.303} = nRT = PV \; for\; ideal\; gas$$

$$4342.16 = 100 \times V_1$$

$$V_1 = \frac{4342.16}{100} = 43.42\; L$$

Example 4: A sample consisting of 2 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.

(a) reversibly

$$-W_{rev} = nRT\, ln\frac{V_2}{V_1} = -2 \times 8.314 \times 295 \times \ln\frac{31.7}{22.8} = 6.82 kJ$$

$$for\; isothermal\; process\; \Delta T = 0 \;\rightarrow\; \Delta U = 0 \rightarrow q = w$$

$$or\; isothermal\; process\; \Delta T = 0 \;\rightarrow\; \Delta H = 0$$

(b) against a constant external pressure

$$-W_{irr} = P\Delta V = P_2(V_2 - V_1)$$

$$P_2 = \frac{nRT}{V_2} = \frac{2 \times 0.0821 \times 295}{31.7} = 1.528\; atm$$

$$-W_{rev} = 1.528 \times 101325\; Nm^{-2}(31.7 - 22.8) \times 10^{-3} m^3 = 1.378\; kJ$$

$$for\; isothermal\; process\; \Delta T = 0 \;\rightarrow\; \Delta U = 0 \rightarrow q = w$$

$$or\; isothermal\; process\; \Delta T = 0 \;\rightarrow\; \Delta H = 0$$

(c) against zero external pressure (W=0)

$$for\; isothermal\; process\; \Delta T = 0 \;\rightarrow\; \Delta U = 0 \rightarrow q = w{=}0,\; \Delta H = 0$$

Example 5: Calculate ΔU, and ΔH when 100 dm^3 of helium at STP are heated in a closed container. Assume that the gas behaves ideally and its C_v is 12.55 J mol^{-1} K^{-1}.

Solution:

$$\Delta U = nC_V\Delta T$$

$$\Delta U = \left(\frac{100}{22.414}mol\right)(12.55\, J\, mol^{-1}K^{-1})(373 - 273\, K)$$

$$= 5226\, J = 5.226\, kJ$$

$$\Delta H = nC_P\Delta T$$

$$= \left(\frac{100}{22.414}mol\right)(12.55 + 8.314\, J\, mol^{-1}K^{-1})(373 - 273\, K)$$

$$= 9317\, J = 9.317\, kJ$$

Example 6: One mole of an ideal gas (C_v = 12.55 J mol^{-1} K^{-1}) at 300 K is compressed adiabatically and reversibly to one fourth its original volume. What is the final temperature of the gas?

Solution:

$$T_1 = 300K \quad , \quad V_1 = 4x \quad , \quad V_2 = x$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\frac{T_2}{300} = \left(\frac{4x}{x}\right)^{\frac{8.314}{12.55}}$$

$$\frac{T_2}{300} = 4^{0.66247} \quad \rightarrow T_2 = 752K$$

Example 6: To what pressure must a given volume of nitrogen at 100 °C and 1 atm be adiabatically compressed in order to raise the temperature to 400 °C. $\gamma = 1.4$

Solution:

$$\left(\frac{T_2}{T_1}\right)\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$\left(\frac{673}{373}\right)\left(\frac{P_2}{1}\right)^{\frac{1.4-1}{1.4}} \quad \rightarrow P_2 = 7.891\, atm$$

Example 7: One mole of nitrogen at 300 K and 20 atm expands to 2 atm. Calculate W, q, Δ*U*, and Δ*H* if expansion were: (Given $C_v = 20.816\ \mathrm{J\ mol^{-1}\ K^{-1}}$)

(1) isothermal and reversible.

(2) isothermal and irreversible.

(3) adiabatic and reversible.

Solution:

(1) For isothermal process $\Delta U = \Delta H = 0$

$$q = -W_{rev} = nRT\ ln\frac{P_1}{P_2} = 1 \times 8.314 \times 300 \times \ln\frac{20}{2} = 5.744kJ$$

(2) For isothermal and irreversible $\Delta U = \Delta H = 0$

$$q = -W_{irr} = P\Delta V = P_2(V_2 - V_1)$$

$$V_1 = \frac{nRT}{P} = \frac{1\ mol\ \times (0.08021) \times 300}{20\ atm} = 1.23\ L$$

$$V_2 = \frac{nRT}{P} = \frac{1\ mol\ \times (0.08021) \times 300}{2\ atm} = 12.3\ L$$

$$q = -W_{irr} = (2 \times 101325\ Nm^{-2})\ (12.31 - 1.23) \times 10^{-3} m^3$$

$$q = -W_{irr} = 2245\ J \rightarrow 2.245kJ/mol$$

(3) Adiabatic reversible expansion:

$$q = 0\ \rightarrow \Delta U = w = nC_V\Delta T$$

$$\left(\frac{T_2}{T_1}\right)\left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}}$$

$$\left(\frac{T_2}{300}\right)\left(\frac{2}{20}\right)^{\frac{8.314}{29.13}}$$

$$T_2 = 150.8K$$

$$\Delta U = w = (1 \times 20.816)(150.8 - 300\ K) = -3.106\ kJ/mol$$

$$\Delta H = nC_P\Delta T = (1 \times 29.13)(150.8 - 300\ K) = -4.346\ kJ/mol$$

Exercises

1- 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.

2- A sample of 4.50 g of methane occupies 12.7 dm^3 at 310 K. (a) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 dm^3. (b) Calculate the work that would be done if the same expansion occurred reversibly.

3- Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from 500 cm^3 at 298.15 K to 2.00 dm^3.

4- Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and 500 cm^3 to a final volume of 3.0 dm^3. $\gamma = 1.3$.

5- Sample of 4.0 mol O_2 is originally confined in 20 dm^3 at 270 K and then undergoes adiabatic expansion against a constant pressure of 600 Torr until the volume has increased by a factor of 3.0. Calculate q, w, ΔT, ΔU, and ΔH. (The final pressure of the gas is not necessarily 600 Torr.)

6- A sample consisting of 1.0 mol of perfect gas molecules with $C_V = 20.8\ J\ K^{-1}$ is initially at 3.25 atm and 310 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and final temperature and the work done.

7- One mole of air at 750K is expanded reversibly and adiabatically from 1 L to 3 L. Taking $C_V = 20.92\ J\ K^{-1}$ and assuming ideal behavior calculate the final temperature, ΔU, ΔH and w.

8- When 229 J of energy is supplied as heat to 3.0 mol Ar(g), the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.