الجامعة التكنولوجية

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الكيمياء الفيزياوية

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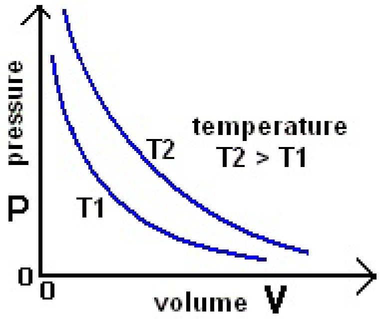
Boyle's Law

According to Boyle's Law, the pressure (P) of a given mass of gas is inversely proportional to its volume (V), provided that the temperature of the gas remains constant.

For an enclosed gas, at constant temperature (T) and mass (n);



$V \alpha \frac{1}{P}$

PV = constant

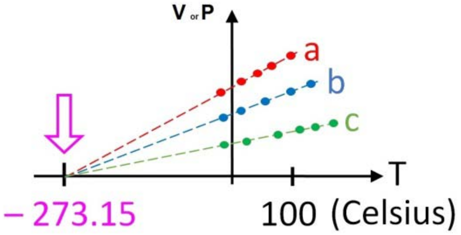
$P_1V_1 = P_2V_2$

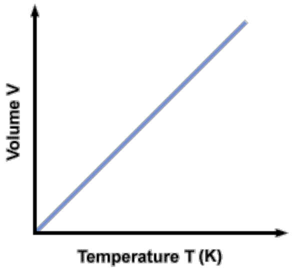
Charles' Law

describes the relationship between volume and temperature of gases at constant pressure and mass, With the same amount of gas he found that as the volume increases the temperature also increases. If the temperature decreases than the volume also decreases

$V \alpha$ T

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



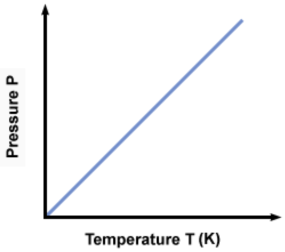


Gay-Lussac's Law

The pressure and absolute temperature (K) of a gas are directly related at constant mass & volume.

$P \alpha$ T

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



Avogadro's Principle

Equal volumes of gases contain equal numbers of molesat constant temp & pressure its true for any ideal gas

$V \alpha n$

$$\frac{v_1}{n_1} = \frac{v_2}{n_2}$$

So $V \alpha \frac{n T}{P}$

$V = \frac{n RT}{P}$ ………………. $PV = nRT$

n = w / Mwt

P Mwt = (w/V) R T

P Mwt = ρ R T

Mwt = ρ (RT / P)

Dalton's Law of Partial Pressures

The total pressure of a mixture of gases equals the sum of the partial pressures of the individual gases.

$P_T = P_1 + P_2 + \ldots.$

$P_T = n_1 \frac{RT}{V} + n_2 \frac{RT}{V}$

$P_1 = \frac{n_1}{n_{1+n_2}} P_T = X_1 P_T$

$P_2 = \frac{n_2}{n_{1+n_2}} P_T = X_2 P_T$ ……..$P_i = X_i P_T$

Amagat law for partial volumes

$V_1 = n_1 \frac{RT}{P}$, $V_2 = n_2 \frac{RT}{P}$, …….

$V_1 + V_2 + V_3 = n_1 + n_2 + n_3 (\frac{RT}{P})$ …….. $Vi = Xi V$

Thermodynamics System and its type

Thermodynamic system (or simply 'system') is a definite macroscopic region or space in the universe, in which one or more thermodynamic processes take place, everything external to a thermodynamic system is called surroundings.
System and surroundings are separated by a definite border called boundary. System, surroundings and boundary constitute the universe.

thermodynamic systems can be broadly classified into three types. They are:

Open System: which allows both mass and energy to flow in and out of it, across its boundary. Example of open system: Water heated in an open container – Here, heat is the energy transferred, water is the mass transferred and container is the thermodynamic system. Both heat and water can pass in and out of the container.

Closed System: A closed system allows only energy (heat and work) to pass in and out of it. It does not allow mass transfer across its boundary

Example of closed system: Water heated in a closed vessel – Here only heat energy can pass in and out of the vessel

Isolated System:An isolated system does not interact with its surroundings. It does not allow both mass and energy transfer across its boundary. It is more restrictive

Zeroth law of Thermodynamic

The zeroth law of thermodynamics states that if two systems, A and B, are in thermal equilibrium with a third system, C, then A and B are in thermal equilibrium with each other. Another way of stating the zeroth law is that every object has a certain temperature, and when two objects are in thermal equilibrium, their temperatures are equal

The First Law of Thermodynamics states that energy can be converted from one form to another with the interaction of heat, work and internal energy, but it cannot be created nor destroyed, under any circumstances. Mathematically, this is represented as

$$\Delta U = q \pm w$$

ΔU is the total change in internal energy of a system,

q is the heat exchanged between a system and its surroundings, and

w is the work done by or on the system.

Work is also equal to the negative external pressure on the system multiplied by the change in volume:

$$W = -P\,\Delta V$$

where P is the external pressure on the system, and ΔV is the change in volume. This is specifically called "pressure-volume" work.

The internal energy of a system would decrease if the system gives off heat or does work. Therefore, internal energy of a system increases when the heat increases (this would be done by adding heat into a system). The internal energy would also increase if work were done onto a system. Any work or heat that goes into or out of a system changes the internal energy. However, since energy is never created nor destroyed (thus, the first law of thermodynamics), the change in internal energy always equals zero. If energy is lost by the system, then it is absorbed by the surroundings. If energy is absorbed into a system, then that energy was released by the surroundings: $\Delta U_{system} = -\Delta U_{surroundings}$

Type of process

Isothermal

An isothermal process is one in which there is no temperature change ($\Delta T = 0$). There may be energy flow into and out of the system, however only the amount required to keep the temperature of the system constant. For Example:

- Phase changes - melting solids and boiling liquids of pure substances requires substantially energy transfer, but does not change temperature.

Adiabatic

An adiabatic process is one in which no heat or mass is transferred between the system and its surroundings ($\Delta m=0$, $\Delta Q=0$). In practice this assumption is most often used for rapidly acting systems (i.e. the thermodynamic process occurs in a short period) or as a method for obtaining conservative results. For example:

Analyzing the stroke of a piston where heat transfer outside of the system can be minimal due to the short period of time analyzed.

Analysis of a combustion reaction using the adiabatic assumption to give an upper limit (conservative) estimate of the flame temperature (referred to as the adiabatic flame temperature).

Isobaric

An isobaric process is one in which the pressure is held constant ($\Delta P=0$). Assuming that the quantity of gas in an isobaric process remains constant the work done by the system is directly promotional to the change in volume or temperature of the system.

The ratio of heat capacity of a gas in an isobaric system with the heat capacity of the gas in an isochoric system makes up the ratio of specific heats for gases $k=Cp/Cv$.

Isochoric

An isochoric system is one in which volume is held constant ($\Delta V=0$). Isochoric processes can also be referred to as isometric or isovolumetric. For Example:

In calorimetry the energy of a reaction may be measured in a "bomb calorimeter". This device does not change volume during the reaction so that the temperature change can be measured as a single variable, and used to calculate the energy released.

infinite. Thus in the limit as the pressure approaches zero, the equation of state assumes the same simple form as for the hypothetical case of B = C = ... = 0; i.e.,

$$Z = 1 \qquad \text{or} \qquad PV = RT$$

We know from the phase rule that the internal energy of a real gas is a function of pressure as well as of temperature. This pressure dependency is the result of forces between the molecules. If such forces did not exist, no energy would be required to alter the average intermolecular distance, and therefore no energy would be required to bring about volume and pressure changes in a gas at constant temperature. We conclude that in the absence of molecular interactions, the internal energy of a gas depends on temperature only. These considerations of the behavior of a hypothetical gas in which no intermolecular forces exist and of a real gas in the limit as pressure approaches zero lead to the definition of an ideal gas as one whose macroscopic behavior is characterized by:

- The equation of state:

$$\boxed{PV = RT} \qquad \textbf{(ideal gas)} \tag{3.13}$$

- An internal energy that is a function of temperature only:

$$\boxed{U = U(T)} \qquad \textbf{(ideal gas)} \tag{3.14}$$

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Implied Property Relations for an Ideal Gas

The definition of heat capacity at constant volume, Eq. (2.16), leads for an ideal gas to the conclusion that C_V is a function of temperature only:

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} = C_V(T) \tag{3.15}$$

The defining equation for enthalpy, Eq. **(2.11)**, applied to an ideal gas, leads to the conclusion that H also is a function of temperature only:

$$H \equiv U + PV = U(T) + RT = H(T) \tag{3.16}$$

The heat capacity at constant pressure C_P, defined by Eq. (2.20), like C_V, is a function of temperature only:

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P = \frac{dH}{dT} = C_P(T) \tag{3.17}$$

A useful relation between C_P and C_V for an ideal gas comes from differentiation of Eq. **(3.16)**:

$$C_P = \frac{dH}{dT} = \frac{dU}{dT} + R = C_V + R \tag{3.18}$$

This equation does not imply that C_P and C_V are themselves constant for an ideal gas, but only that they vary with temperature in such a way that their difference is equal to R.

For any change of state of an ideal gas Eq. **(3.15)** may be written:

$$dU = C_V\,dT \tag{3.19a}$$

Whence,

$$\Delta U = \int C_V \, dT \tag{3.19b}$$

By Eq. (3.17),

$$dH = C_P \, dT \tag{3.20a}$$

Whence,

$$\Delta H = \int C_P \, dT \tag{3.20b}$$

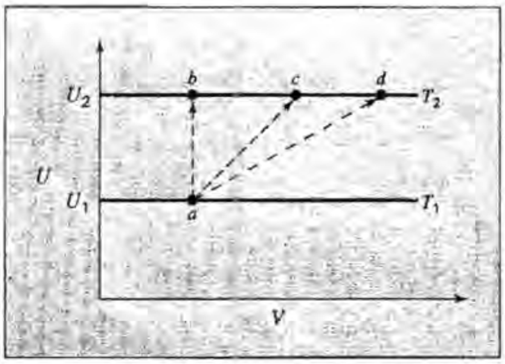

Figure 3.5 Internal energy changes for an ideal gas

Since both the internal energy and C_V of an ideal gas are functions of temperature only, ΔU for an ideal gas is *always* given by Eq. (3.19b), regardless of the kind of process causing the change. This is demonstrated in Fig. 3.5, which shows a graph of internal energy as a function of molar volume with temperature as parameter. Since U is independent of V, a plot of U vs. V at constant temperature is a horizontal line. For different temperatures, U has different values, with a separate line for each temperature. Two such lines are shown in Fig. 3.5, one for temperature T_1 and one for a higher temperature T_2. The dashed line connecting points a and b represents a constant-volume process for which the temperature increases from T_1 to T_2 and the internal energy changes by $\Delta U = U_2 - U_1$. This change in internal energy is given by Eq. (3.19b) as $\Delta U = \int C_V \, dT$. The dashed lines connecting points a and c and points a and d represent other processes not occurring at constant volume but which also lead from an initial temperature T_1 to a final temperature T_2. The graph shows that the change in U for these processes is the same as for the constant-volume process, and it is therefore given by the same equation, namely, $\Delta U = \int C_V \, dT$. However, ΔU is *not* equal to Q for these processes, because Q depends not only on T_1 and T_2 but also on the path of the process. An entirely analogous discussion applies to the enthalpy H of an ideal gas. (See Sec. 2.16.)

The ideal gas is a model fluid described by simple *property relations*, which are frequently good approximations when applied to actual gases. In *process calculations*, gases at pressures up to a few bars may often be considered ideal, and simple equations then apply.

Equations for Process Calculations: Ideal Gases

For an ideal gas in any mechanically reversible closed-system process, Eq. (2.6), written for a unit mass or a mole, may be combined with Eq. (3.19a):

$$dQ + dW = C_V \, dT$$

The work for a mechanically reversible closed-system process is given by Eq. (1.2), also written for one mole or a unit mass:

$$dW = -P\,dV$$

Whence, $$dQ = C_V\,dT + P\,dV$$

The two preceding equations for an ideal gas undergoing a reversible process in a closed system take several forms through elimination of one of the variables P, V, or T by Eq. (3.13). Thus, with $P = RT/V$ they become:

$$dQ = C_V\,dT + RT\frac{dV}{V} \tag{3.21}$$

$$dW = -RT\frac{dV}{V} \tag{3.22}$$

Alternatively, let $V = RT/\mathrm{P}$:

$$dQ = C_V\,dT + P\left(\frac{R}{P}dT - \frac{RT}{P^2}dP\right)$$

With Eq. (3.18) this reduces to:

$$dQ = C_P\,dT - RT\frac{dP}{P} \tag{3.23}$$

Also, $$dW = -R\,dT + RT\frac{dP}{P} \tag{3.24}$$

Finally, let $T = PV/R$:

$$dQ = C_V\left(\frac{V}{R}dP + \frac{P}{R}dV\right) + P\,dV$$

Again with Eq. (3.18) this becomes:

$$dQ = \frac{C_V}{R}V\,dP + \frac{C_P}{R}P\,dV \tag{3.25}$$

The work is simply: $$dW = -P\,dV$$

These equations may be applied to various processes, as described in what follows. The general restrictions implicit in their derivation are:

- The equations are valid for ideal gases.

- The process is mechanically reversible.
- The system is closed.

Isothermal Process

By Eqs. (3.19b) and (3.20b), $\Delta U = \Delta H = 0$

By Eqs. (3.21) and (3.23), $Q = RT\ln\frac{V_2}{V_1} = -RT\ln\frac{P_2}{P_1}$

By Eqs. (3.22) and (3.24), $W = -RT\ln\frac{V_2}{V_1} = RT\ln\frac{P_2}{P_1}$

Note that $Q = -W$, a result that also follows from Eq. (2.3). Therefore,

$$Q = -W = RT\ln\frac{V_2}{V_1} = -RT\ln\frac{P_2}{P_1} \qquad (\text{const } T) \qquad (3.26)$$

Isobaric Process

By Eqs. (3.19b) and (3.20b),

$$AU = \int C_V\,dT \qquad \text{and} \qquad \Delta H = \int C_P\,dT$$

and by Eqs. (3.23) and (3.24),

$$Q = \int C_P\,dT \qquad \text{and} \qquad W = -R(T_2 - T_1)$$

Note that $Q = AH$, a result also given by Eq. (2.13). Therefore,

$$Q = \Delta H = \int C_P\,dT \qquad (\text{const } P) \qquad (3.27)$$

Isochoric (Constant-V) Process

Equations (3.19b) and (3.20b) again apply:

$$\Delta U = \int C_V\,dT \qquad \text{and} \qquad AH = \int C_P\,dT$$

By Eqs. (3.21) and (1.3),

$$Q = \int C_V\,dT \qquad \text{and} \qquad W = 0$$

Note that $Q = AU$, a result also given by Eq. (2.10). Therefore,

$$Q = \Delta U = \int C_V\,dT \qquad (\text{const } V) \qquad (3.28)$$

Adiabatic Process: Constant Heat Capacities

An adiabatic process is one for which there is no heat transfer between the system and its surroundings; that is, $dQ = 0$. Each of Eqs. (3.21), (3.23), and (3.25) may therefore be set equal to zero. Integration with C_V and C_P constant then yields simple relations among the variables T, P, and V. For example, Eq. (3.21) becomes:

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

Integration with C_V constant then gives:

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

Similarly, Eqs. (3.23) and (3.25) lead to:

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

These equations may also be expressed as:

$$\boxed{\begin{aligned} TV^{\gamma-1} &= \text{constant} && (3.29a)\\ TP^{(1-\gamma)/\gamma} &= \text{constant} && (3.29b)\\ PV^{\gamma} &= \text{constant} && (3.29c) \end{aligned}}$$

Where by *definition*,[3]

$$\boxed{\gamma \equiv \frac{C_P}{C_V}} \qquad (3.30)$$

Equations (3.29) apply to an ideal gas with constant heat capacities undergoing a mechanically reversible adiabatic process.

The work of an adiabatic process may be obtained from the relation:

$$dW = dU = C_V\,dT$$

If C_V is constant, integration gives:

$$W = \Delta U = C_V\,\Delta T \qquad (3.31)$$

Alternative forms of Eq. (3.31) are obtained when C_V is eliminated in favor of the heat-capacity ratio γ:

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$$

---

[3] If C_V and C_P are constant, γ is necessarily constant. For an ideal gas, the assumption of constant γ is equivalent to the assumption that the heat capacities themselves are constant. This is the only way that the ratio $C_P/C_V \equiv \gamma$ and the difference $C_P - C_V = R$ can *both* be constant. Except for the monotonic gases, both C_P and C_V actually increase with temperature, but the ratio γ is less sensitive to temperature than the heat capacities themselves.

Whence, $$C_V = \frac{R}{\gamma - 1}$$

Therefore $$W = C_V\,\Delta T = \frac{R\,\Delta T}{\gamma - 1}$$

Since $RT_1 = P_1V_1$ and $RT_2 = P_2V_2$, this expression may be written:

$$W = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \tag{3.32}$$

Equations (3.31) and (3.32) are general for an adiabatic process, whether reversible or not. However, V_2 is usually not known, and is eliminated from Eq. (3.32) by Eq. (3.29c), valid only for mechanically reversible processes. This leads to the expression:

$$W = \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] \tag{3.33}$$

The same result is obtained when the relation between P and V given by Eq. (3.29c) is used for integration of the expression $W = -\int P\,dV$.

Equations (3.29), (3.31), (3.32), and (3.33) are for ideal gases with constant heat capacities. Equations (3.29) and (3.33) also require the process to be mechanically reversible; processes which are adiabatic but not mechanically reversible are ***not*** described by these equations.

When applied to real gases, Eqs. (3.29) through (3.33) often yield satisfactory approximations, provided the deviations from ideality are relatively small. For monatomic gases, y = 1.67; approximate values of y are 1.4 for diatomic gases and 1.3 for simple polyatomic gases such as CO_2, SO_2, NH_3, and CH_4.

Polytropic Process

Since ***polytropic*** means "turning many ways:' ***polytropic process*** suggests a model of some versatility. With 6 a constant, it is defined as a process for which

$$PV^{\delta} = \text{constant} \tag{3.34a}$$

For an ideal gas equations analogous to Eqs. (3.29a) and (3.29b) are readily derived:

$$TV^{\delta-1} = \text{constant} \tag{3.34b}$$

and $$TP^{(1-\delta)/\delta} = \text{constant} \tag{3.34c}$$

When the relation between P and V is given by Eq. (3.34a), evaluation of $\int P\,dV$ yields Eq. (3.33) with y replaced by 6:

$$W = \frac{RT_1}{\delta - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right] \tag{3.35}$$

Moreover, for constant heat capacities, the first law solved for Q yields:

$$Q = \frac{(\delta - \gamma)RT_1}{(\delta - 1)(\gamma - 1)}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right] \tag{3.36}$$

The several processes already described correspond to the four paths shown on Fig. 3.6 for specific values of 6:

- Isobaric process: By Eq. (3.34a), $6 = 0$.
- Isothermal process: By Eq. (3.34b), $6 = 1$.
- Adiabatic process: $6 = \gamma$.
- Isochoric process: By Eq. (3.34a), $dV/dP = V/P\delta$; for constant V, $6 = \pm\infty$.

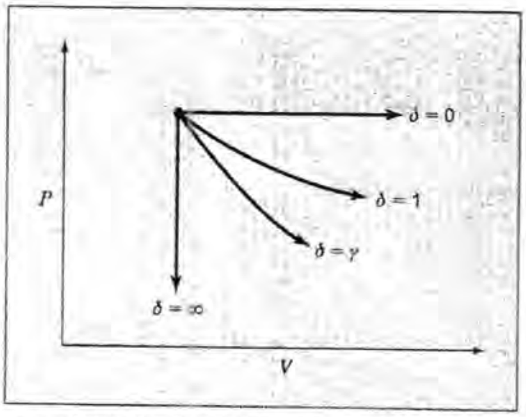

Figure 3.6 Paths of polytropic processes characterized by specific values of 6

Irreversible Process

The equations developed in this section have been derived for mechanically reversible, closed-system processes for ideal gases. However, those equations which relate changes in state functions only are valid for ideal gases regardless of the process. They apply equally to reversible and irreversible processes in both closed and open systems, because changes in state functions depend only on the initial and final states of the system. On the other hand, an equation for Q or W is specific to the process considered in its derivation.

The work of an irreversible process is calculated by a two-step procedure. First, W is determined for a mechanically reversible process that accomplishes the same change of state as the actual irreversible process. Second, this result is multiplied or divided by an efficiency to give the actual work. If the process produces work, the absolute value for the reversible process is too large and must be multiplied by an efficiency. If the process requires work, the value for the reversible process is too small and must be divided by an efficiency.

Applications of the concepts and equations developed in this section are illustrated in the examples that follow. In particular, the work of irreversible processes is treated in the last part of Ex. 3.3.

Example 3.2

Air is compressed from an initial condition of 1 bar and 298.15 K (25°C) to a final state of 5 bar and 298.15 K (25°C) by three different mechanically reversible processes in a closed system:

(*a*) Heating at constant volume followed by cooling at constant pressure.
(*b*) Isothermal compression.
(*c*) Adiabatic compression followed by cooling at constant volume.

Assume air to be an ideal gas with the constant heat capacities, $C_V = (5/2)R$ and $C_P = (7/2)R$. Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air for each process.

Solution 3.2

Choose the system as 1 mol of air, contained in an imaginary frictionless piston/cylinder arrangement. For $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$C_V = 20.785 \qquad C_P = 29.099 \text{ J mol}^{-1} \text{ K}^{-1}$$

The initial and final conditions of the air are identical with those of Ex. 2.9, where the molar volumes are given as:

$$V_1 = 0.024\,79 \qquad V_2 = 0.004\,958 \text{ m}^3$$

Moreover, since the initial and final temperatures are the same, then for all parts of the problem:

$$\Delta U = \Delta H = 0$$

(*a*) The heat transferred, from Ex. 2.9(*b*), is $Q = -9915$ J. Thus by the first law applied to the entire process:

$$W = \Delta U - Q = 0 + 9915 = 9915 \text{ J}$$

(*b*) Equation (3.26) for the isothermal compression of an ideal gas applies here:

$$Q = -W = RT \ln \frac{P_1}{P_2} = (8.314)(298.15) \ln \frac{1}{5} = -3990 \text{ J}$$

(*c*) The initial adiabatic compression of the air takes it to its final volume of $0.004\,958 \text{ m}^3$. By Eqs. (3.29a) and (3.29c), the temperature and pressure at this point are:

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma - 1} = (298.15)\left(\frac{0.024\,79}{0.004\,958}\right)^{0.4} = 567.57 \text{ K}$$

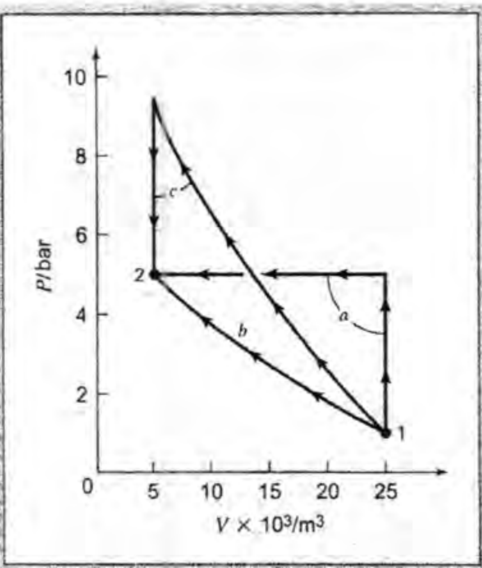

Figure 3.7 Diagram for Ex. 3.2

$$P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma} = (1)\left(\frac{0.024\,79}{0.004\,958}\right)^{1.4} = 9.52 \text{ bar}$$

For this step $Q = 0$, and by Eq. (3.31),

$$W = C_V\,\Delta T = (20.785)(567.57 - 298.15) = 5600 \text{ J}$$

For the second step at constant V, $W = 0$. For the overall process,

$$W = 5600 + 0 = 5600 \text{ J}$$

Moreover, $\Delta U = 0$, and by the first law,

$$Q = \Delta U - W = 0 - 5600 = -5600 \text{ J}$$

Although the property changes ΔU and ΔH are zero for each process, Q and W are path-dependent. Figure 3.7 shows each process on a PV diagram. Since the work for each of these mechanically reversible processes is given by $W = -\int P\,dV$, the work for each process is proportional to the total area below the paths on the PV diagram representing the process. The relative sizes of these areas correspond to the numerical values of W.

Example 3.3

An ideal gas undergoes the following sequence of mechanically reversible processes in a closed system:

(a) From an initial state of 343.15 K (70°C) and 1 bar, it is compressed adiabatically to 423.15 K (150°C).

(*b*) It is then cooled from 423.15 to 343.15 K (150 to 70°C) at constant pressure.
(*c*) Finally, it is expanded isothermally to its original state.

Calculate W, Q, ΔU, and ΔH for each of the three processes and for the entire cycle. Take $C_V = (3/2)R$ and $C_P = (5/2)R$.

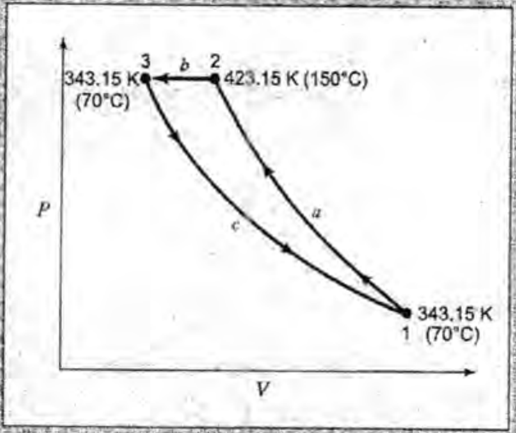

Figure 3.8 Diagram for Ex. 3.3

If these processes are carried out *irreversibly* but so as to accomplish exactly the same *changes of state* (i.e., the same changes in P, T, U, and H), then different values of Q and W result. Calculate Q and W if each step is carried out with an efficiency of 80%.

Solution 3.3

From the given information,

$$C_V = (3/2)(8.314) = 12.471 \text{ J mol}^{-1} \text{ K}^{-1}$$
$$C_P = (5/2)(8.314) = 20.785 \text{ J mol}^{-1} \text{ K}^{-1}$$

The cycle is represented on a PV diagram in Fig. 3.8. Consider first the mechanically reversible operation of the cycle, and take as a basis 1 mol of gas.

(*a*) For an ideal gas undergoing adiabatic compression, $Q = 0$, and

$$\Delta U = W = C_V\,\Delta T = (12.471)(423.15 - 343.15) = 998 \text{ J}$$
$$\Delta H = C_P\,\Delta T = (20.785)(423.15 - 343.15) = 1663 \text{ J}$$

Pressure P_2 can be found from Eq. (3.29b):

$$P_2 = P_1\left(\frac{T_2}{T_1}\right)^{\gamma/(\gamma-1)} = (1)\left(\frac{423.15}{343.15}\right)^{2.5} = 1.689 \text{ bar}$$

(*b*) Equation (3.27), applicable to the constant-pressure process, gives:

$$Q = \Delta H = C_P\,\Delta T = (20.785)(343.15 - 423.15) = -1663 \text{ J}$$

Also, for an ideal gas,

$$\Delta U = C_V\,\Delta T = (12.471)(343.15 - 423.15) = -998\ \mathrm{J}$$

By the first law,

$$W = \Delta U - Q = -998 - (-1663) = 665\ \mathrm{J}$$

(c) For ideal gases undergoing an isothermal process, ΔU and ΔH are zero; Eq. (3.26) yields:

$$Q = -W = RT\ln\frac{P_3}{P_1} = RT\ln\frac{P_2}{P_1} = (8.314)(343.15)\ln\frac{1.689}{1} = 1495\ \mathrm{J}$$

For the entire process,

$$\begin{aligned} Q &= 0 - 1663 + 1495 = -168\ \mathrm{J} \\ W &= 998 + 665 - 1495 = 168\ \mathrm{J} \\ \Delta U &= 998 - 998 + 0 = 0 \\ \Delta H &= 1663 - 1663 + 0 = 0 \end{aligned}$$

The property changes ΔU and ΔH both are zero for the entire cycle, because the initial and final states are identical. Note also that $Q = -W$ for the cycle. This follows from the first law with $\Delta U = 0$.

If the same changes of state are carried out by irreversible processes, the property changes for the steps are identical with those already calculated. However, the values of Q and W change.

(*a*) This step can no longer be adiabatic. For mechanically reversible, adiabatic compression, $W = 998$ J. If the process is 80% efficient compared with this,

$$W = \frac{998}{0.80} = 1248\ \mathrm{J}$$

Since ΔU is still 998 J, by the first law:

$$Q = \Delta U - W = 998 - 1248 = -250\ \mathrm{J}$$

(*b*) The work for the mechanically reversible cooling process is 665 J. For the irreversible process,

$$W = \frac{665}{0.80} = 831\ \mathrm{J}$$

and $$Q = \Delta U - W = -998 - 831 = -1829\ \mathrm{J}$$

(*c*) As work is done *by* the system in this step, the irreversible work in absolute value is less than the reversible work:

$$W = (0.80)(-1495) = -1196\ \mathrm{J}$$

and $$Q = \Delta U - W = 0 + 1196 = 1196 \text{ J}$$

For the entire cycle, ΔU and ΔH are again zero, but

$$Q = -250 - 1829 + 1196 = -883 \text{ J}$$

and $$W = 1248 + 831 - 1196 = 883 \text{ J}$$

A summary of these results is given in the accompanying table. All values are in joules.

	Mechanically reversible				Irreversible			
	ΔU	ΔH	Q	W	ΔU	ΔH	Q	W
(*a*)	998	1663	0	998	998	1663	−250	1248
(*b*)	−998	−1663	−1663	665	−998	−1663	−1829	831
(*c*)	0	0	1495	−1495	0	0	1196	−1196
Sum	0	0	−168	168	0	0	−883	883

The cycle is one which requires work and produces an equal amount of heat. The striking feature of the comparison shown in the table is that the total work required when the cycle consists of three irreversible steps is more than five times the total work required when the steps are mechanically reversible, even though each irreversible step is assumed 80% efficient.

Example 3.4

A 0.4 kg mass of nitrogen at 300.15 K (27°C) is held in a vertical cylinder by a frictionless piston. The weight of the piston makes the pressure of the nitrogen 0.35 bar higher than that of the surrounding atmosphere, which is at 1 bar and 300.15 K (27°C). Thus the nitrogen is initially at a pressure of 1.35 bar, and is in mechanical and thermal equilibrium with its surroundings. Consider the following sequence of processes:

(*a*) The apparatus is immersed in an ice/water bath and is allowed to come to equilibrium.

(*b*) A variable force is slowly applied to the piston so that the nitrogen is compressed reversibly at the constant temperature of 273.15 K (0°C) until the gas volume reaches one-half the value at the end of step (*a*). At this point the piston is held in place by latches.

(*c*) The apparatus is removed from the ice/water bath and comes to thermal equilibrium with the surrounding atmosphere at 300.15 K (27°C).

(*d*) The latches are removed, and the apparatus is allowed to return to complete equilibrium with its surroundings.

Sketch the entire cycle on a PV diagram, and calculate Q, W, ΔU^t, and ΔH^t for the nitrogen for each step of the cycle. Nitrogen may be considered an ideal gas for which $C_V = (5/2)R$ and $C_P = (7/2)R$.

Solution 3.4

At the end of the cycle the nitrogen returns to its initial conditions of 300.15 K (27°C) and 1.35 bar. The steps making up the cycle are:

$$(a) \qquad 300.15\text{ K }(27^\circ\text{C}),\ 1.35\text{ bar} \xrightarrow{\text{const}P} 273.15\text{ K }(0^\circ\text{C}),\ 1.35\text{ bar}$$

$$(b) \qquad 273.15\text{ K }(0^\circ\text{C}),\ V_2 \xrightarrow{\text{const}T} 273.15\text{ K }(0^\circ\text{C}),\ V_3 = \tfrac{1}{2}V_2$$

$$(c) \qquad 273.15\text{ K }(0^\circ\text{C}),\ V_3 \xrightarrow{\text{const}V} 300.15\text{ K }(27^\circ\text{C}),\ V_4 = V_3$$

$$(d) \qquad 300.15\text{ K }(27^\circ\text{C}),\ P_4 \xrightarrow{T_4=T_1} 300.15\text{ K }(27^\circ\text{C}),\ 1.35\text{ bar}$$

Nitrogen has a molar mass $M = 28$; the number of moles comprising the system is therefore:

$$n = \frac{m}{M} = \frac{0.4 \times 1000}{28} = 14.286 \text{ mol}$$

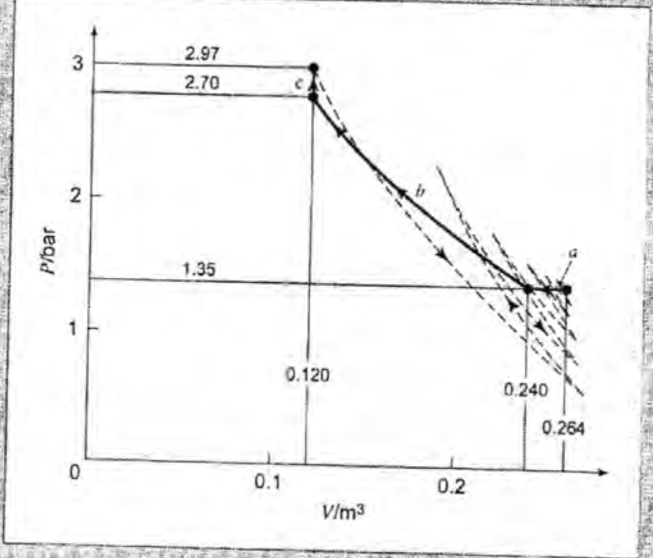

Figure 3.9 Diagram for Ex. 3.4

(a) In this step, represented by the horizontal line marked a in Fig. 3.9, the nitrogen is cooled at constant pressure. The process is mechanically reversible, even though the heat transfer occurs irreversibly as the result of a finite temperature difference. Thus, with $R = 8.314$ J mol^{-1} K^{-1},

$$W_a = -n \int P\,dV = -nP\,\Delta V = -nR\,\Delta T$$

or $$W_a = -(14.286)(8.314)(273.15 - 300.15\ \text{K}) = 3207\ \text{J}$$

By Eq. (2.23),

$$Q_a = n\,\Delta H_a = nC_P\,\Delta T_a = (14.286)(7/2)(8.314)(273.15 - 300.15) = -11\,224\ \text{J}$$

From the first law,

$$n\,\Delta U_a = Q_a + W_a = -11\,224 + 3207 = -8017\ \text{J}$$

(*b*) The process carried out here is an isothermal compression shown by curve *b* in Fig. 3.9, and for which:

$$\Delta U_b = \Delta H_b = 0$$

Assume the compression to be mechanically reversible; then,

$$Q_b = -W_b = nRT\ln\frac{V_3}{V_2} = (14.286)(8.314)(273.15)\ln\frac{1}{2} = -22\,487\ \text{J}$$

(c) For this constant-volume process, $W_c = 0$ and, according to Eq. (2.19):

$$Q_c = n\,\Delta U_c = nC_V\,\Delta T_c = (14.286)(5/2)(8.314)(300.15 - 273.15) = 8017\ \text{J}$$

In addition,

$$n\,\Delta H_c = nC_P\,\Delta T_c = (14.286)(7/2)(8.314)(300.15 - 273.15) = 11\,224\ \text{J}$$

(*d*) The first three steps of the cycle can be sketched on a PV diagram without difficulty, because their paths are known. For the final step this is not possible, because the process is irreversible. When the latches holding the frictionless piston are removed, the piston moves rapidly upward, and owing to its inertia goes beyond its equilibrium position. This initial expansion approximates a reversible, adiabatic process, because little turbulence results from a single stroke of the piston and because heat transfer is relatively slow. The subsequent oscillations of the piston as it gradually reaches its final equilibrium position are the primary source of the irreversibility, because they cause turbulence and mixing in both the gas and the atmosphere. This process goes on for a considerable time during which heat transfer occurs in an amount sufficient to return the nitrogen to its initial temperature of 300.15 K (27°C) at a pressure of 1.35 bar. It is not possible to specify the exact path of an irreversible process and this makes impossible the calculation of either Q or W. However, the dashed lines in Fig. 3.9 suggest the form that it takes.

Unlike work and heat, the property changes of the system for step *d* can be computed, since they depend solely on the initial and final states, and these are known. Both ΔU_d and ΔH_d are zero, because the initial and final temperatures are 300.15 K (27°C). The first law applies to irreversible as well as to reversible processes, and for step *d* it becomes:

$$\Delta U_d = Q_d + W_d = 0$$

whence $$Q_d = -W_d$$

Although neither Q_d nor W_d can be calculated, their absolute values are the same. Step d results in elevation of the piston and the atmosphere, and a compensating decrease in the internal energy of the surrounding atmosphere.

Example 3.5

Air flows at a steady rate through a horizontal insulated pipe which contains a partly closed valve. The conditions of the air upstream from the valve are 293.15 K (20°C) and 6 bar, and the downstream pressure is 3 bar. The line leaving the valve is enough larger than the entrance line so that the kinetic-energy change of the air as it flows through the valve is negligible. If air is regarded as an ideal gas, what is the temperature of the air some distance downstream from the valve?

Solution 3.5

Flow through a partly closed valve is known as a *throttling process*. The line is insulated, making Q small; moreover, the potential-energy and kinetic-energy changes are negligible. Since no shaft work is accomplished, $W_s = 0$. Hence, Eq. (2.32) reduces to: $\Delta H = 0$. Thus, for an ideal gas,

$$\Delta H = \int_{T_1}^{T_2} C_P\,dT = 0$$

Whence, $$T_2 = T_1$$

The result that $\Delta H = 0$ is general for a throttling process, because the assumptions of negligible heat transfer and potential- and kinetic-energy changes are usually valid. If the fluid is an ideal gas, no temperature change occurs. The throttling process is inherently irreversible, but this is immaterial to the calculation, because Eq. (3.20b) is valid for an ideal gas whatever the process.

Example 3.6

If in Ex. 3.5 the flow rate of the air is 1 mol s^{-1} and if the pipe has an inner diameter of 5 cm, both upstream *and* downstream from the valve, what is the kinetic-energy change of the air and what is its temperature change? For air, $C_P = (7/2)R$ and the molar mass is $M = 29$ g mol^{-1}.

Solution 3.6

Velocity is found from Eq. (2.24b):

$$u = \frac{\dot{n}}{A\rho} = \frac{\dot{n}V}{A}$$

where $$A = \frac{\pi}{4}D^2 = \left(\frac{\pi}{4}\right)(5 \times 10^{-2})^2 = 1.964 \times 10^{-3}\ \text{m}^2$$

The upstream molar volume as given by the ideal-gas equation is:

$$V_1 = \frac{RT_1}{P_1} = \frac{(83.14)(293.15)}{6} \times 10^{-6} = 4.062 \times 10^{-3}\ \text{m}^3\ \text{mol}^{-1}$$

Then, $$u_1 = \frac{(1)(4.062 \times 10^{-3})}{1.964 \times 10^{-3}} = 2.069 \text{ m s}^{-1}$$

If the downstream temperature is little changed from the upstream temperature, then to a good approximation:

$$V_2 = 2V_1 \qquad \text{and} \qquad u_2 = 2u_1 = 4.138 \text{ m s}^{-1}$$

The rate of change in kinetic energy is therefore:

$$\begin{aligned} \dot{m}\,\Delta(\tfrac{1}{2}u^2) &= \dot{n}M\,\Delta(\tfrac{1}{2}u^2) \\ &= (1 \times 29 \times 10^{-3})\frac{(4.138^2 - 2.069^2)}{2} = 0.186 \text{ J s}^{-1} \text{ or W} \end{aligned}$$

In the absence of heat transfer and work, the energy balance, Eq. (2.31), becomes:

$$\Delta(H + \tfrac{1}{2}u^2)\dot{m} = \dot{m}\,\Delta H + \dot{m}\,\Delta(\tfrac{1}{2}u^2) = 0$$

$$\dot{m}\frac{C_P}{M}\Delta T + \dot{m}\,\Delta(\tfrac{1}{2}u^2) = \dot{n}C_P\,\Delta T + \dot{m}\,\Delta(\tfrac{1}{2}u^2) = 0$$

Whence $$(1)(7/2)(8.314)\Delta T = -\dot{m}\,\Delta(\tfrac{1}{2}u^2) = -0.186$$

and $$\Delta T = -0.0064 \text{ K}$$

Clearly, the initial assumption is justified: the temperature change across the valve is negligible. Even for an upstream pressure of 10 bar and a downstream pressure of 1 bar and for the same flow rate, the temperature change is only -0.076 K. We conclude that, except for very unusual conditions, $\Delta H = 0$ is a satisfactory energy balance for a throttling process.

3.4 APPLICATION OF THE VIRIAL EQUATIONS

The two forms of the virial expansion given by Eqs. (3.11) and (3.12) are infinite series. For engineering purposes their use is practical only where convergence is very rapid, that is, where two or three terms suffice for reasonably close approximations to the values of the series. This is realized for gases and vapors at low to moderate pressures.

Figure 3.10 shows a compressibility-factor graph for methane. Values of the compressibility factor Z (as calculated from PVT data for methane by the defining equation $Z = PV/RT$) are plotted vs. pressure for various constant temperatures. The resulting isotherms show graphically what the virial expansion in P is intended to represent analytically. All isotherms originate at the value $Z = 1$ for $P = 0$. In addition the isotherms are nearly straight lines at low pressures. Thus the tangent to an isotherm at $P = 0$ is a good approximation of the isotherm from $P \to 0$ to some finite pressure. Differentiation of Eq. (3.11) for a given temperature gives:

$$\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \cdots$$