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The basic concepts

- ► Two parts of the universe in physical chemistry

System vs Surroundings

System : the part of the world in which we have a special interest

Surroundings : the region outside the system where we make our measurement

- ► Three types of the system :

(a) open system (b) closed system (c) isolated system

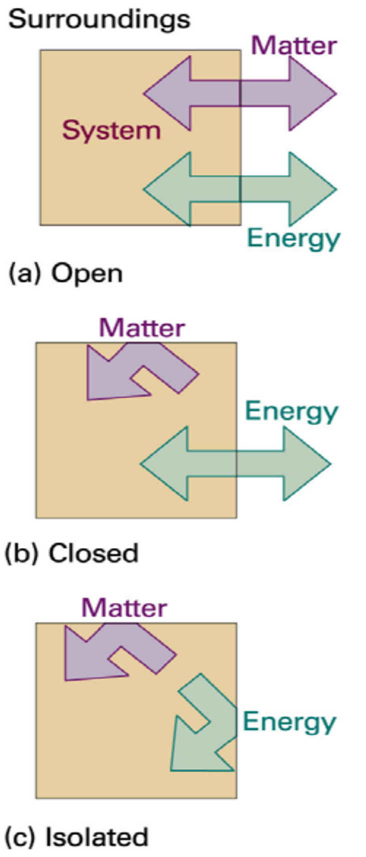


Fig. 2.1 (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.

2.1 Work, Heat and Energy

► **Energy** : the capacity (or ability) to do work

► **Work, *w*** : a way to transfer energy

- It is done on an object when the object is moved due to an external force or against an opposing force.
- Doing work is equivalent to raising a weight somewhere in the surroundings.

► **Heat, *q*** : A measure of thermal energy transfer

- Diathermic: a boundary that permits energy transfer as heat
- Adiabatic: a boundary that does not permit energy transfer as heat
- Exothermic: releasing energy as heat
- Endothermic: absorbing energy as heat

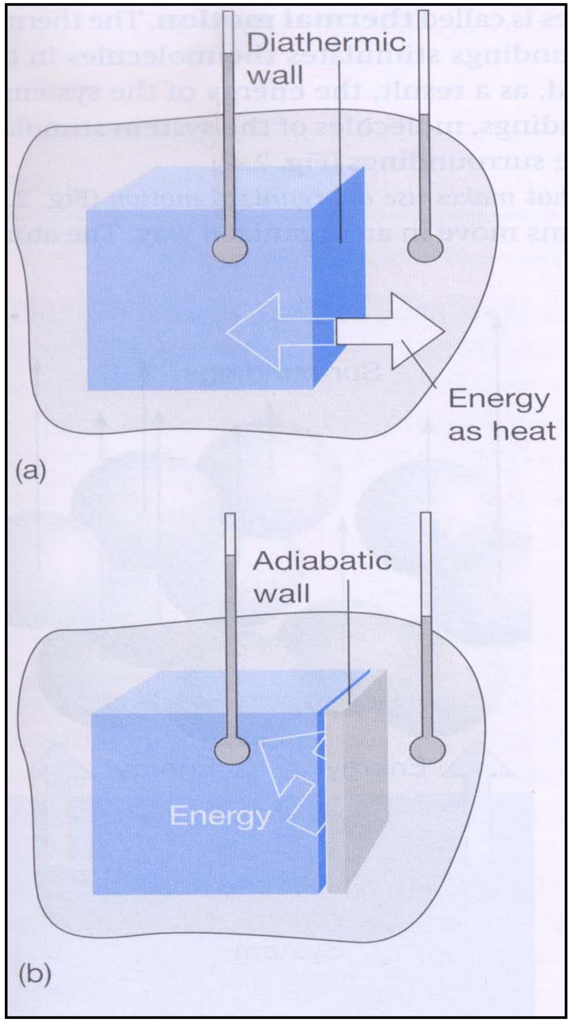
Unit of Work, Heat, and Energy: J (joule) in SI

1 J = 1 $\mathrm{kgm^2s^{-2}}$, 1 eV= 1.6×10^{-19} J, 1 cal = 4.184 J

2.1 Work, Heat and Energy

(a) A diathermic system is one that allows energy to escape as heat through its boundary if there is a difference in temperature between the system and its surroundings

(b) An adiabatic system is one that does not permit the passage of energy as heat thorough its boundary even if there is a temperature difference between the system and its surroundings



Diathermic & adiabatic system

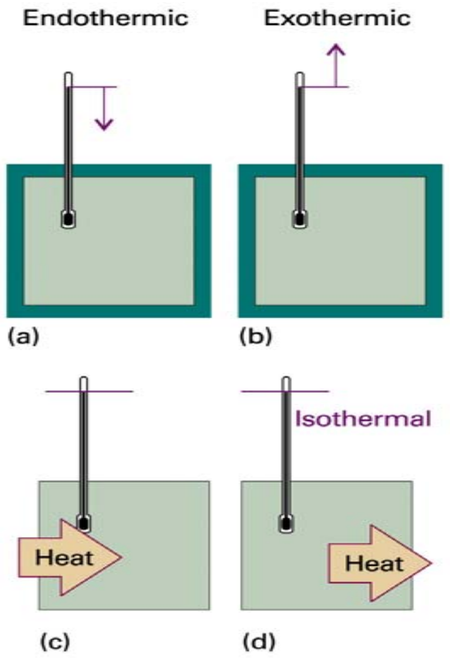


Fig. 2.2 (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, then energy leaves as heat, and the process is isothermal.

Endothermic & exothermic system

2.1 Work, Heat and Energy

Molecular interpretation 2.1

- ► **Heat is defined as energy transfer making use of thermal motion in the surrounding**

- ► **Work is defined as energy transfer making use of the organized motion of atoms in the surroundings**

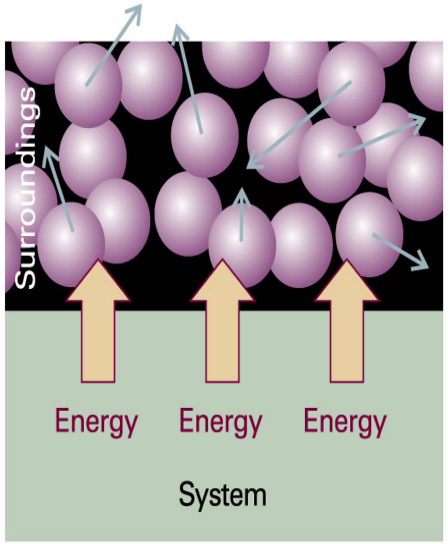


Fig. 2.3 When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

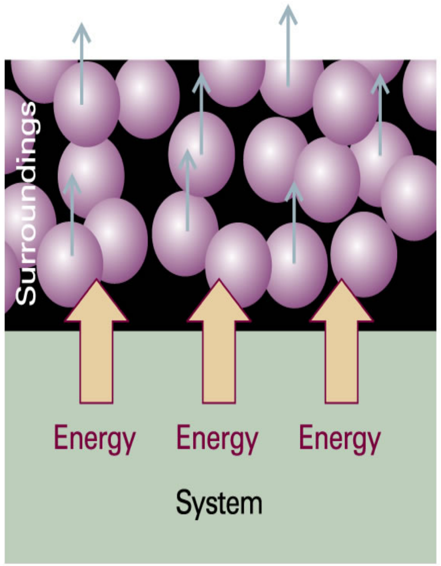


Fig. 2.4 When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

2.2 The internal energy, U

► **Thermodynamics: the study of the transformations of energy**

► **The First Law : The internal energy of an isolated system is constant**
Evidence? No perpetual motion machine (a machine that does work without consuming fuel or some other source of energy)

► **Internal energy, *U***

- **Internal energy : the total energy of a system in thermodynamics (i.e., the total kinetic and potential energy of the molecules in the system)**
- **The change in internal energy, $\Delta U = U_f - U_i$**
  Where, U_i and U_f are the internal energies at an initial and a final state, respectively
- **A state function in the sense that its value depends only on the current state of the system**
- **An extensive property (dependent on the amount of substance in the sample)**
  cf) intensive property

2.2 The internal energy

Molecular interpretation 2.2 The internal energy of gas

Equipartition theorem of classical mechanics : Useful guide to the average energy associated with each degree of freedom.

Kinetic energy of a moving atom of mass m, E_K

$$\boxed{E_k = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2}$$

At thermal equilibrium (i.e., at a given temperature, T of a system), the average value of each quadratic contribution to the energy is identical and equal to (1/2)kT for a collected particles

Since the mean thermal energy of the atoms is (3/2)kT and the total energy of the gas is (3/2)NkT (or (3/2)nRT)

Internal energy of a gas, U_m

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

where $U_m(0)$ is the molar internal energy at $T = 0$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$ for a perfect gas

2.2 The internal energy

Molecular interpretation 2.2 (continued)

ex) Polyatomic molecules should be taken into account the effect of rotation & vibration (N_2, CO_2)

$$\boxed{U_m = U_m(0) + \frac{5}{2}RT}$$

- linear molecule

ex) CH_4 or H_2O

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

- nonlinear molecule

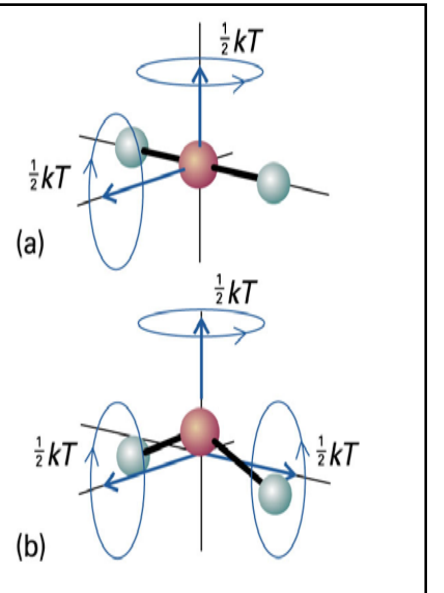


Fig. 2.5 The rotational modes of molecules and the corresponding average energies at a temperature *T*. (a) A linear molecule can rotate about two axes perpendicular to the line of the atoms. (b) A nonlinear molecule can rotate about three perpendicular axes.

2.2 The first law of thermodynamics

► First Law of thermodynamics

- Mathematical statement of the First Law

$$\boxed{\Delta U = q + w}$$

- In an isolated system, q = 0 and w = 0, thus ΔU = 0 (i.e., U = constant)

- In a closed system

If energy is transferred to the system as work or heat, $w > 0$ or $q > 0$

If energy is lost from the system as work or heat, $w < 0$ or $q < 0$

2.3 Expansion Work

(a) The general expression for the work

The work required to move an object a distance *dz* against an opposing force of magnitude *F*

$$dw = -F\,dz \quad ; \quad F = p_{ex}A$$

$$dw = -p_{ex}A\,dz$$

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

$$w = -\int_{V_i}^{V_f} p_{ex}\,dV$$

w : work

P_{ex} : external pressure

F : force acting on the outer face of piston

A : Area

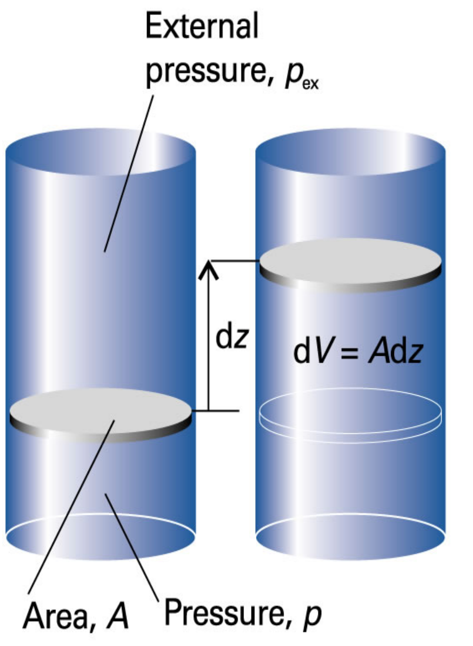


Fig. 2.6 When a piston of area A moves out through a distance dz, it sweeps out a volume d$V = A$dz. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex}A$.

2.3 Expansion Work

(b) Free expansion

Expansion against zero opposing force

$w = 0$ since $p_{ex} = 0$

(c) Expansion against constant pressure

The external pressure is constant throughout the expansion

$|w|$ is equal to the area (blue) in p-V graph

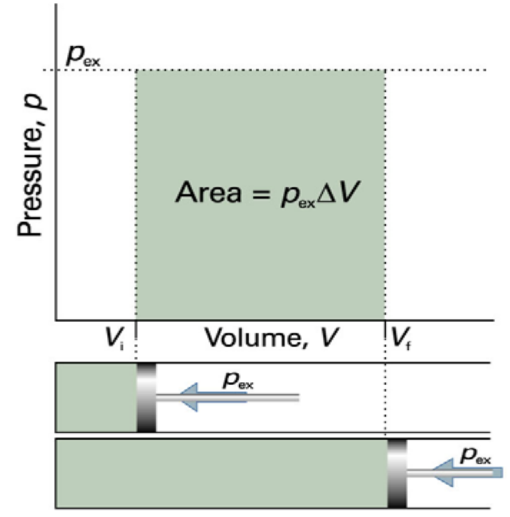


Fig. 2.7 The work done by a gas when it expands against a constant external pressure, p_{ex}, is equal to the shaded area in this example of an indicator diagram.

$$w = -\int_{V_i}^{V_f} p_{ex} dV = -p_{ex}(V_f - V_i)$$

$$w = -p_{ex}\Delta V \quad \text{since} \;\; \Delta V = V_f - V_i$$

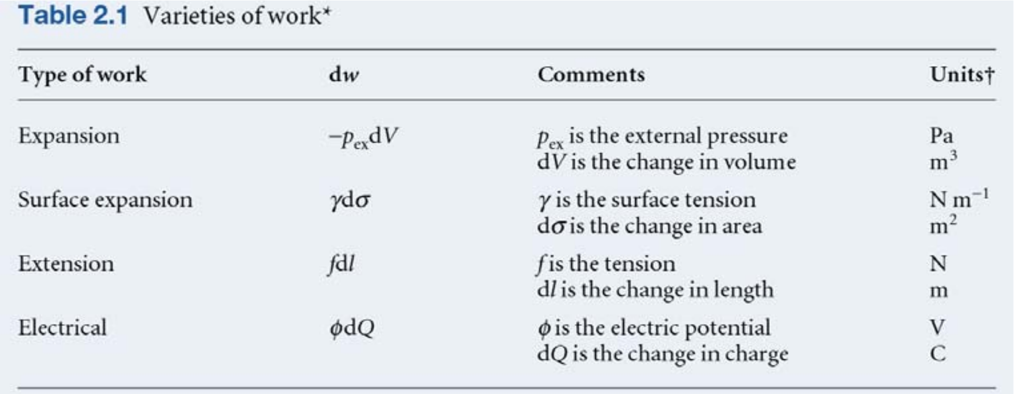


Table 2.1 Varieties of work*

Type of work	dw	Comments	Units†
Expansion	$-p_{ex}dV$	p_{ex} is the external pressure dV is the change in volume	Pa m^3
Surface expansion	$\gamma d\sigma$	γ is the surface tension $d\sigma$ is the change in area	$N\,m^{-1}$ m^2
Extension	fdl	f is the tension dl is the change in length	N m
Electrical	ϕdQ	ϕ is the electric potential dQ is the change in charge	V C

2.3 Expansion Work

(d) Reversible expansion

Reversible change : a change that can be reversed by an infinitesimal modification of variable

Equilibrium : if an infinitesimal change in the conditions in opposite directions results in opposite changes in its state

Set $p_{ex} = p$ at each stage of the reversible expansion

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

Total work for reversible expansion

$$\boxed{w = -\int_{V_i}^{V_f} pdV}$$

2.3 Expansion Work

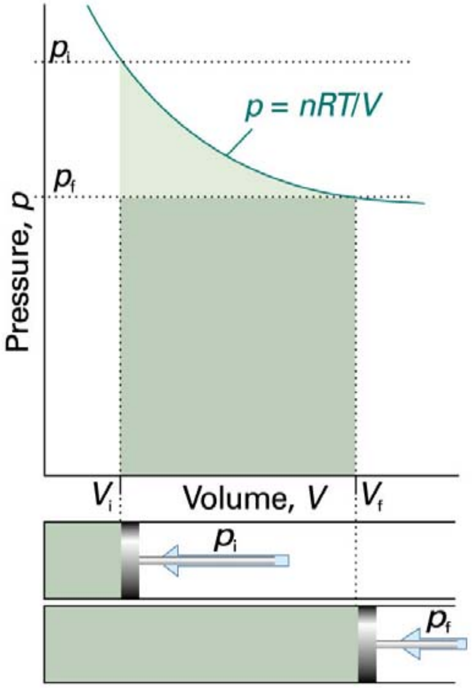


Fig. 2.8 The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$. The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work is greater than the irreversible work.

(e) Isothermal reversible expansion

For a perfect gas

$$\boxed{p = \frac{nRT}{V}}$$

V : volume at each stage

n, R, T : constant

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

Maximum work with reversible expansion

(Increasing p_{ex} → compression)

2.4 Heat transactions

In general, the change in internal energy of a system

$$\boxed{dU = dq + dw_{\mathrm{exp}} + dw_e}$$

where, dw_{exp} = the expansion work

dw_e = work in addition to the expansion work

If $dw_{exp} = dw_e = 0$,

$dU = dq$ (at constant volume, no additional work)

Thus, $\Delta U = q_v$

$q_v > 0$: measuring the energy supplied to a system at constant volume

$q_v < 0$: measuring the energy obtained from a system at constant volume

2.4 Heat transactions

Heat Capacity

► **Two type of heat capacities**

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$ **: heat capacity at constant volume**

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$ **: heat capacity at constant pressure**

- extensive property
- molar heat capacity at constant volume, $C_{v,m}$: intensive property
- specific heat capacity (informally, specific heat) : the heat capacity of the sample divided by the mass

► **In a constant-volume system**

$dU = C_v dT$

► **If C_v is independent of T over the range of temperature of interest**

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

► **At the phase transition temperature, the heat capacity of a sample is infinite**

2.4 Heat transactions

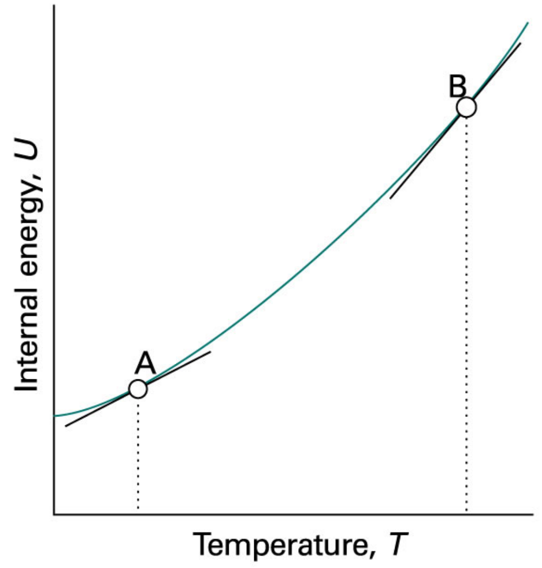


Fig. 2.10 The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system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

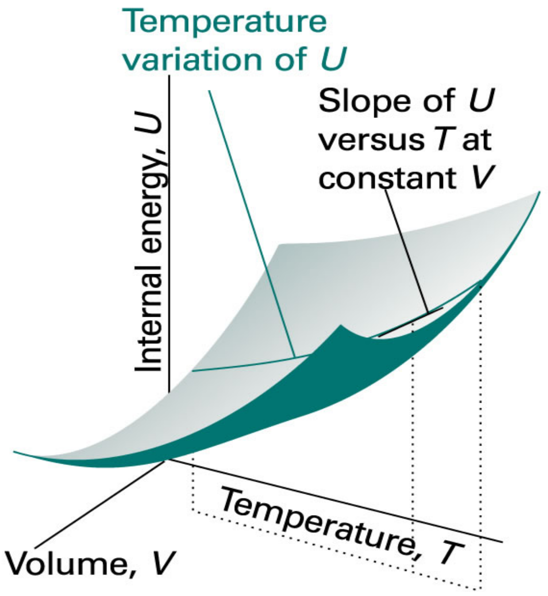


Fig. 2.11 The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface. The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to T. The slope of this curve at any point is the partial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

2.5 Enthalpy

Consider a system exhibiting free change in volume at constant pressure due to heat supply from surroundings

- Some thermal energy is returned to surroundings as expansion work → $dU < dq$
- The heat supplied to the system at constant pressure is equal to the change in the enthalpy

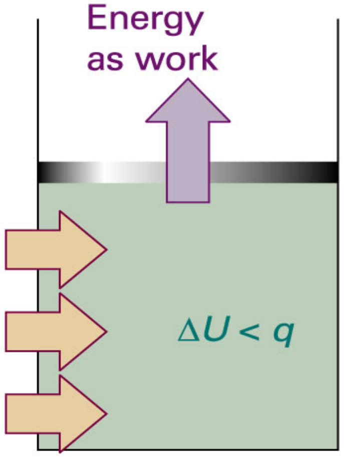


Fig. 2.12 When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

(a) Definition of enthalpy: H = U + pV

ΔH is the state function.

$dH = dU + d(pV) = dU + pdV + Vdp$

$dH = dU + pdV + Vdp$

Since $dU = dq + dw$ and $dw = - pdV$ for expansion work at constant pressure

$dH = dq + Vdp$

At constant p,

$\Delta H = q_p$

2.5 Enthalpy

(b) The measurement of an enthalpy change, ΔH

Calorimeters

DSC (differential scanning calorimeter)

(c) The variation of enthalpy with temperature

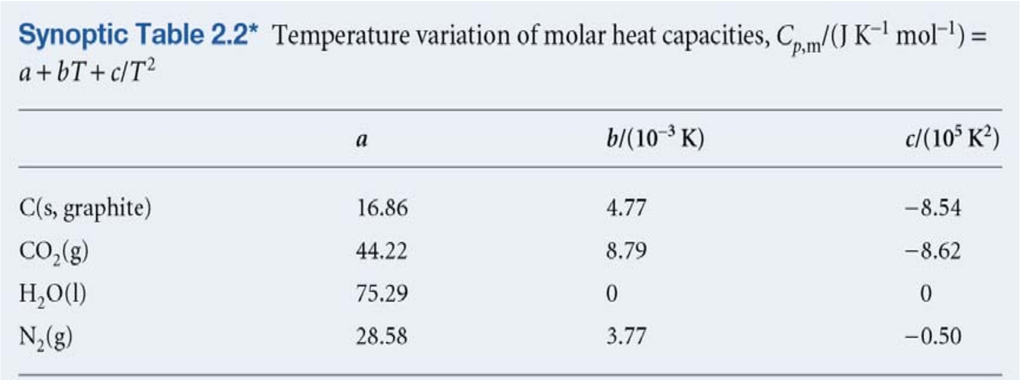
- **Heat capacity at constant pressure, $C_p = (\partial H/\partial T)_p$**
- **Molar heat capacity at constant *p*, $C_{p,m}$**

At constant *p*, $dH = C_p dT$

If *Cp* is independent of *T* over the range of temperatures of interest, $\Delta H = C_p \Delta T$

- **A convenient approximate empirical expression**

$$C_{p,m} = a + bT + c/T^2$$



Synoptic Table 2.2* Temperature variation of molar heat capacities, $C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}}) = a + bT + c/T^2$

	a	$b/(10^{-3}\ \mathrm{K})$	$c/(10^5\ \mathrm{K}^2)$
C(s, graphite)	16.86	4.77	−8.54
CO_2(g)	44.22	8.79	−8.62
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77	−0.50

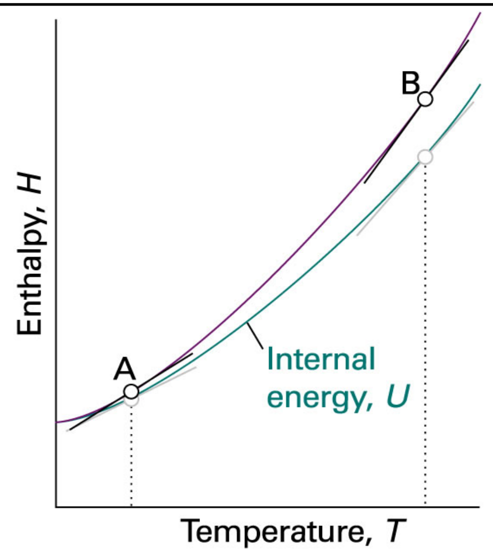


Fig. 2.14 The slope of the tangent to a curve of the enthalpy of a system subjected to a constant pressure plotted against temperature is the constant-pressure heat capacity. The slope may change with temperature, in which case the heat capacity varies with temperature. Thus, the heat capacities at A and B are different. For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and $C_{p,\mathrm{m}}$ is larger than $C_{V,\mathrm{m}}$.

2.6 Adiabatic change

Changes occur when a perfect gas expands adiabatically.

(Work is done. No heat enters the system)

The internal energy fall.

A decrease in temperature should be expected.

$$\Delta U = C_v (T_f - T_i) = C_V \Delta T \qquad q = 0, \Delta U = q + w$$

$$w_{ad} = C_V \Delta T$$

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c} \qquad c = C_{V,m} / R$$

$$V_i T_i^c = V_f T_f^c$$ (VT^c=constant)

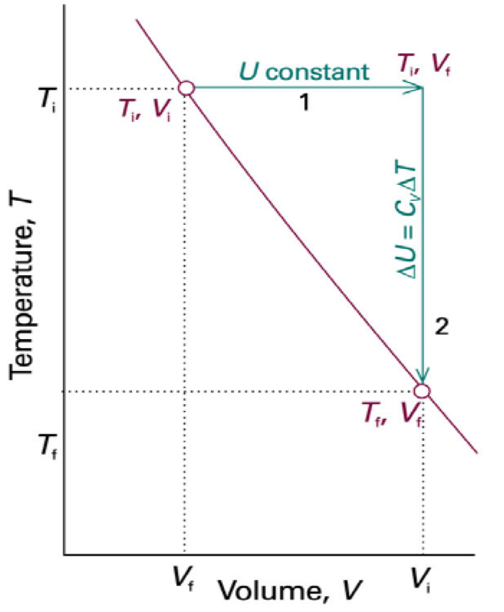


Fig. 2.17 To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas. In the second step, the temperature of the system is reduced at constant volume. The overall change in internal energy is the sum of the changes for the two steps.

2.6 Adiabatic change

- The pressure of a perfect gas that undergoes reversible adiabatic expansion from a volume V_i to a volume V_f

$$p_f V_f^{\gamma} = p_i V_i^{\gamma} \qquad \gamma = C_{p,m} / C_{V,m}$$

- For a monatomic perfect gas

$$C_{V,m} = \frac{3}{2}R, \quad C_{p,m} = \frac{5}{2}R, \quad \gamma = \frac{5}{3}$$

- For a gas of nonlinear polyatomic molecules

$$C_{V,m} = 3R, \qquad \gamma = \frac{4}{3}$$

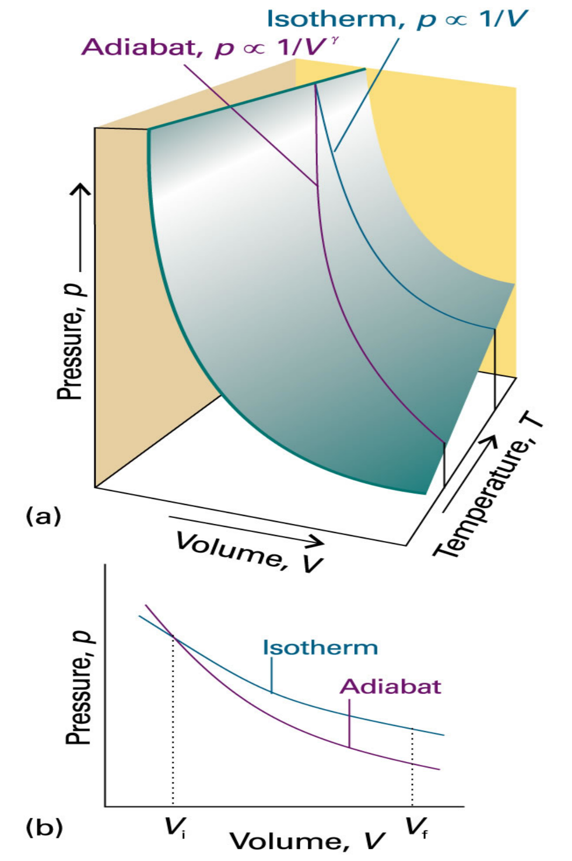


Fig. 2.18 An adiabat depicts the variation of pressure with volume when a gas expands adiabatically. (a) An adiabat for a perfect gas undergoing reversible expansion. (b) Note that the pressure declines more steeply for an adiabat than it does for an isotherm because the temperature decreases in the former.