Classical and Statistical Thermodynamics

Statistical thermodynamics: machinery for interrelating the statistical properties of a mechanical system containing a very large number of particles.
Once this machinery is developed, we can obtain some very general results that do not depend on the exact details of the statistical treatment. These results take the form of general statements regarding heat and work, and are usually referred to as classical thermodynamics. Historically, classical thermodynamics was the first type of thermodynamics to be discovered. In fact, for many years, the laws of classical thermodynamics seemed rather mysterious, because their statistical justification had yet to be discovered. The strength of classical thermodynamics is its great generality, which comes about because it does not depend on any detailed assumptions about the statistical properties of the system under investigation. This generality is also the principle weakness of classical thermodynamics. Only a relatively few statements can be made on such general grounds, so many interesting properties of the system remain outside the scope of classical thermodynamics. If we go beyond classical thermodynamics, and start to investigate the statistical machinery that underpins it, then we get all of the results of classical thermodynamics, plus a large number of other results that enable the macroscopic parameters of the system to be calculated from a knowledge of its microscopic constituents. This approach is known as statistical thermodynamics, and is extremely powerful. The only drawback is that the further we delve inside the statistical machinery of thermodynamics, the harder it becomes to perform the necessary calculations. Note that both classical and statistical thermodynamics are only valid for systems in equilibrium. If the system is not in equilibrium then the problem becomes considerably more difficult (irreversible thermodynamics).

Fundamental concepts

Thermodynamical systems

System: part of the universe within some closed surface called boundary.

State of the system is specified by the values of measurable state properties.

Microscopic system: roughly of atomic dimensions, or smaller.

Macroscopic system: large enough to be visible in the ordinary sense.

Isolated system: no interchange of energy with the surroundings.

Closed system: no matter crosses the boundary.

Open system: there is an interchange of matter with the surroundings.

Extensive properties: proportional to the mass of the system (example: energy)

Intensive properties: independent of the mass (examples: temperature, pressure)

Specific properties

The specific value of extensive property: a ratio of the value of the property to the mass of the system <=> value per unit mass.

Specific volume = 1/Density:

$$v = \frac{V}{m} = \frac{1}{\rho}$$

Specific values are of course intensive properties.

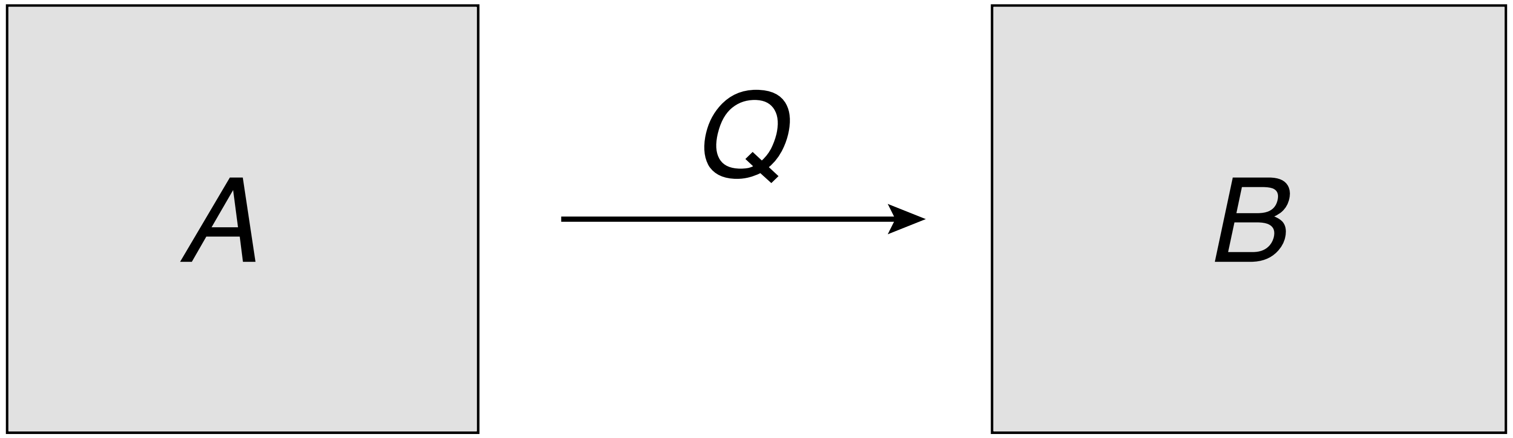
Modal specific value of the property: ratio of the value of the property to the number of moles of the system.

1 kmol (kilomole) = mass in kilograms numerically equal to the molecular weight, for example, 32 kg for O_2 . 1 mol (mole) = 10^{-3} kmol

1 mol = mass of N_A molecules. Avogadro number $N_A = 6.022 \times 10^{23}$

Temperature and thermal equilibrium

Consider two macroscopic objects that are isolated from the rest of the universe, but are in contact with each other.



$$T_A > T_B$$

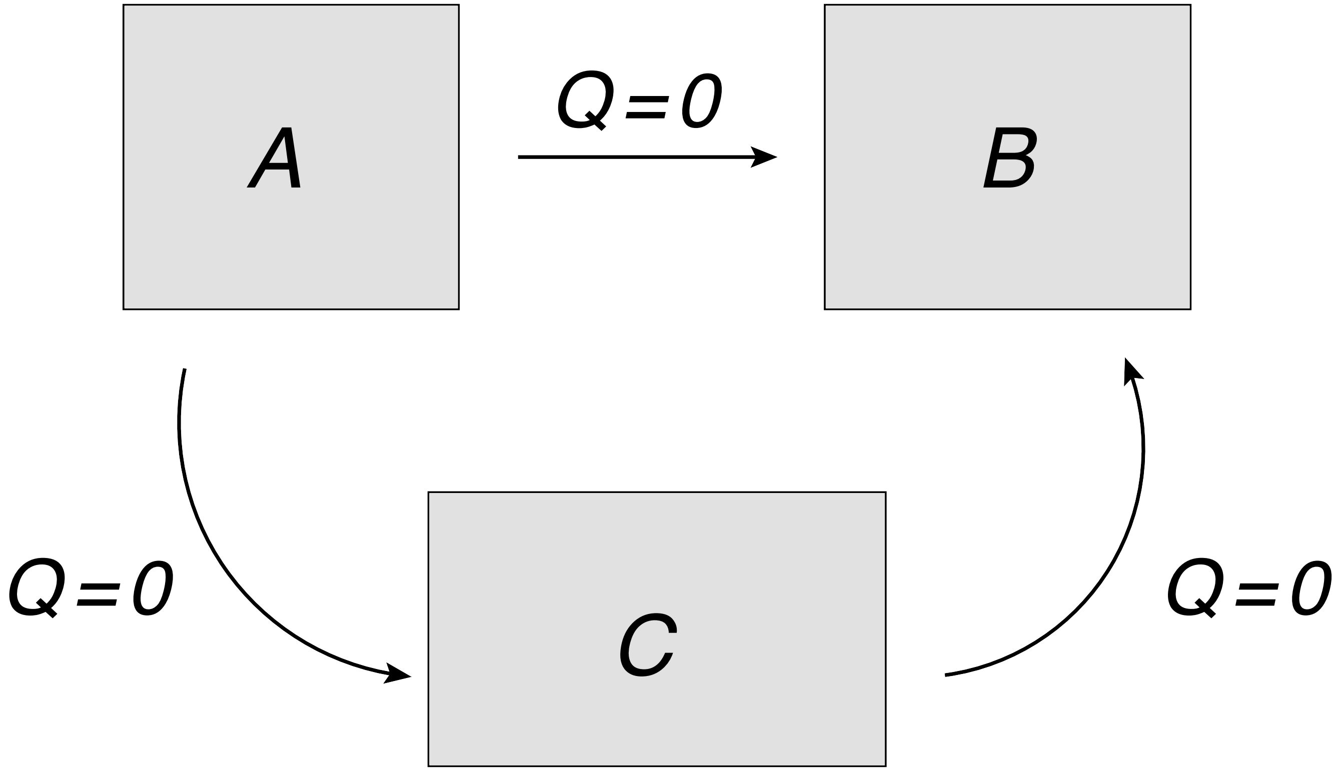
We say that block A has a higher temperature than block B if the energy (heat) flows from A to B. After the lapse of some time, called the relaxation time, the flow of energy from A to B ceases. At this point the two blocks are in thermal equilibrium with each other, and we would say that they have the same temperature.

Heat

The word heat refers to energy that is transferred, or energy that flows, spontaneously due to a difference in temperature. We often say heat flows into a system or out of a system, as for instance heat flowed from block A to block B above. It is incorrect to say that heat resides in a system, or that a system contains a certain amount of heat.

There are three mechanisms of energy transfer: conduction, convection, and radiation. Two objects, or two systems, are said to be in contact if energy can flow from one to the other. The most obvious example is two blocks sitting side by side, literally touching. However, another example is the Sun and the Earth, exchanging energy by radiation. The Sun has the higher temperature, so there is a net flow of energy from the Sun to the Earth. The Sun and the Earth are in contact.

“Zeroth law” of thermodynamics



$$T_A = T_B = T_C$$

When any two bodies are each separately in thermal equilibrium with a third, they are also in thermal equilibrium with each other.

The rate at which the thermal equilibrium is approached depends on the nature of the boundary of the system

Adiabatic boundary: no heat flow from the surroundings
Diathermal boundary: no temperature difference with the surroundings

Kelvin scale of temperature

Temperature scale is defined by two points.

First point - absolute zero. The temperature at which the pressure of a dilute gas at fixed volume would go to zero is called the absolute zero temperature.

Second point - triple point the temperature at which ice, liquid water, and vapor are in thermal equilibrium

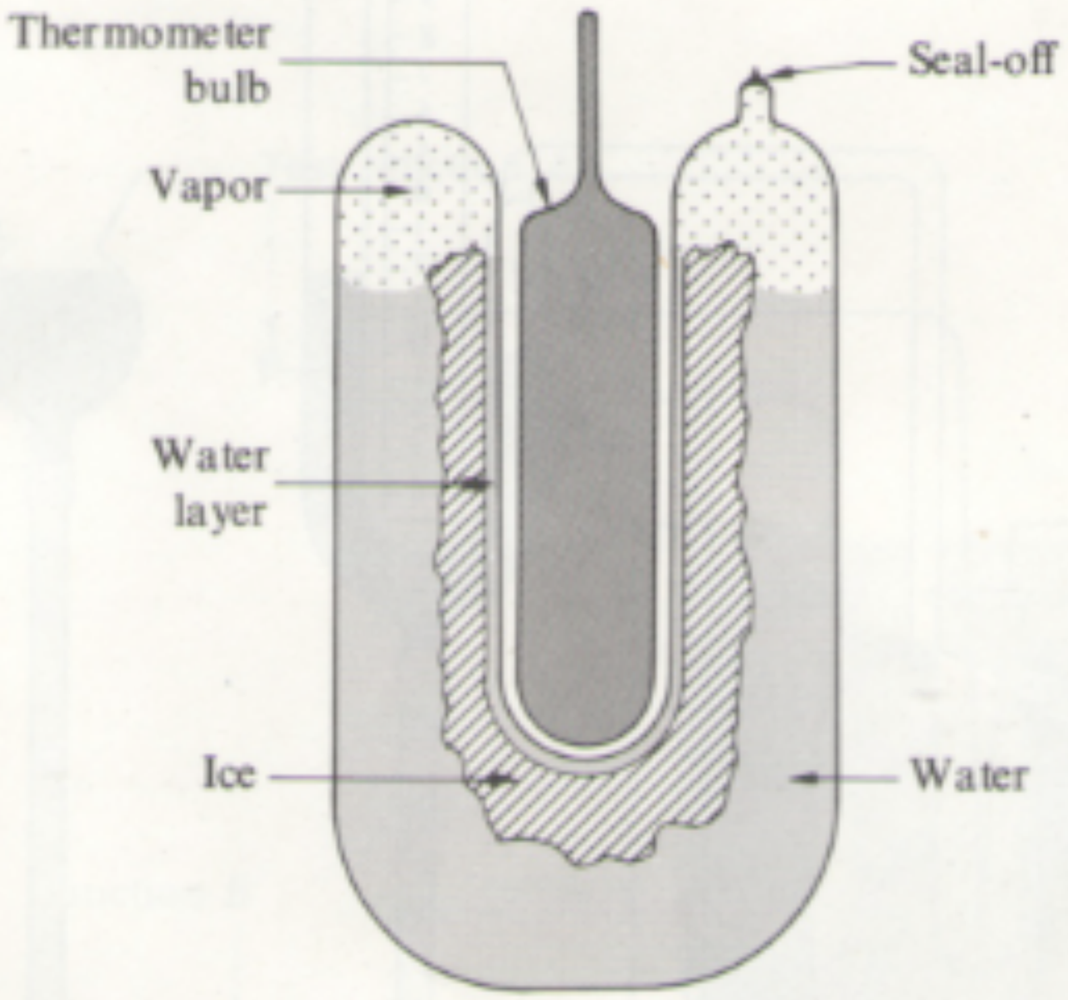


Fig. 1–3 Triple-point cell with a thermometer in the well, which melts a thin layer of ice nearby.

By convention, the zero point is 0 K and the triple point is 273.15 K

1 K = 1 C

Thermodynamical equilibrium

Mechanical equilibrium

If there are variations of pressure, or stress or parts of the system may move. Eventually this motion ceases and the system is in mechanical equilibrium.

Chemical equilibrium

The system may contain different substances undergoing chemical reactions. Eventually, all chemical reactions cease and the system is in chemical equilibrium.

Thermodynamical equilibrium

A system which is in thermal, mechanical, and chemical equilibrium is said to be in thermodynamical equilibrium.

Processes

Quasistatic process: at any moment the system departs form an equilibrium only infinitesimally. A quasistatic process is a succession of equilibrium states.

Isochoric process: volume of the system is constant.

Isobaric process: pressure in the system is constant.

Isothermal process: temperature of the system is constant.

Adiabatic process: no flow of heat thru the boundary.

Reversible process: whose direction can be reversed by a set of infinitesimal changes.

Example

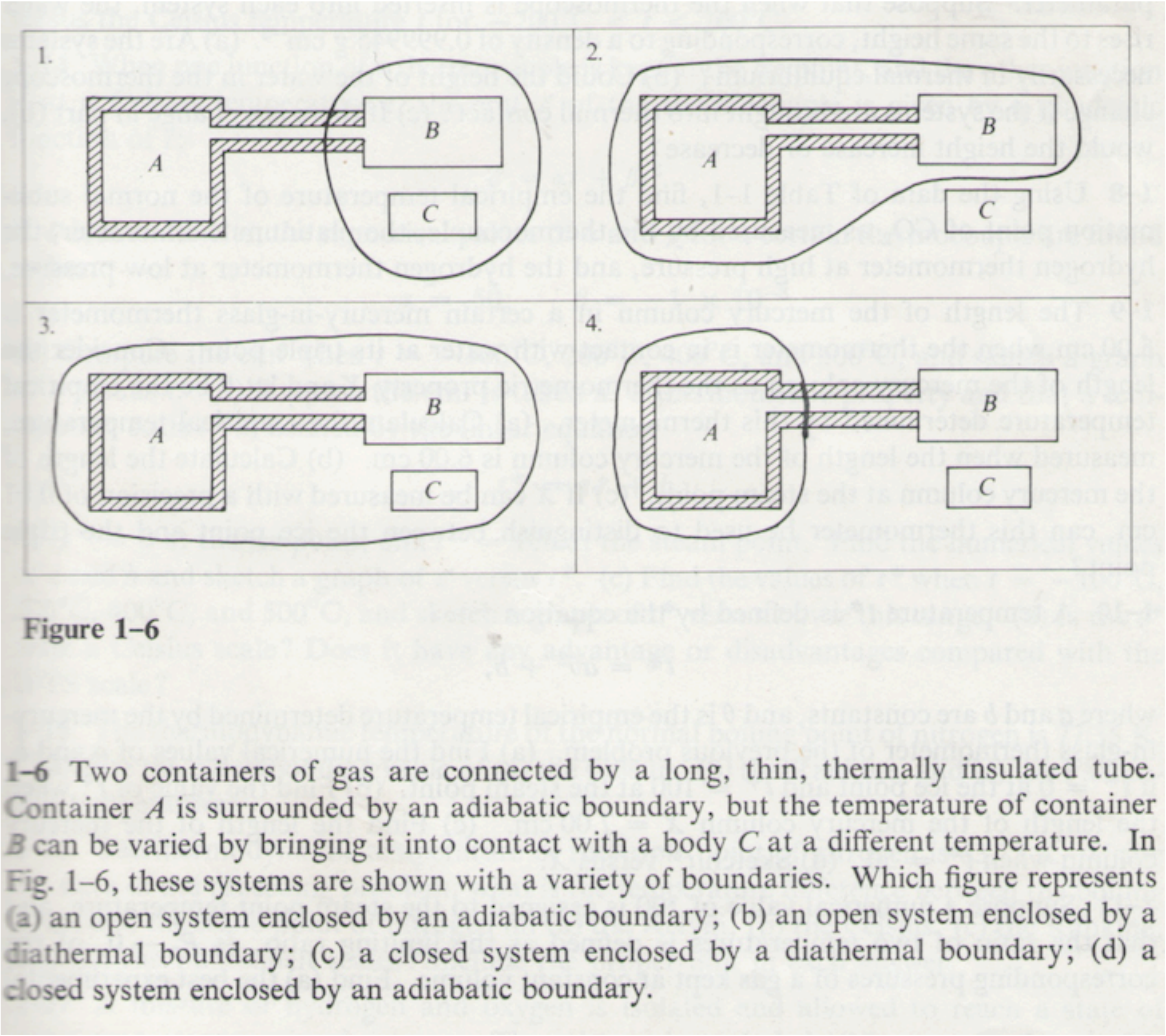


Figure 1–6

1–6 Two containers of gas are connected by a long, thin, thermally insulated tube. Container A is surrounded by an adiabatic boundary, but the temperature of container B can be varied by bringing it into contact with a body C at a different temperature. In Fig. 1–6, these systems are shown with a variety of boundaries. Which figure represents (a) an open system enclosed by an adiabatic boundary; (b) an open system enclosed by a diathermal boundary; (c) a closed system enclosed by a diathermal boundary; (d) a closed system enclosed by an adiabatic boundary.

Equations of State

Equation of state

$$f(P, V, T, m) = 0$$

Example: equation of state of an ideal gas: $PV = NkT$

$$N = \text{number of molecules}, \quad k = 1.38 \times 10^{-23}\,\frac{\text{J}}{\text{K}} \equiv \text{Boltzmann constant}$$

The equation of state can be written in the form that depends only on the nature of the substance rather than on how much of the substance is present:

$$f(P, v, T) = 0$$

Example: $Pv = RT \quad \Leftrightarrow \quad pV = nRT$

In SI units

$$PV = (\text{number of moles})RT, \qquad R = kN_A = 8.31\,\frac{\text{JK}^{-1}}{\text{mol}} = 8.31 \times 10^3\,\frac{\text{JK}^{-1}}{\text{kmol}}$$

$$\Leftrightarrow \quad Pv = RT$$

R: universal gas constant

Equation of state of an ideal gas

$$Pv = RT \Leftrightarrow PV = nRT$$

n: number of moles

R: universal gas constant

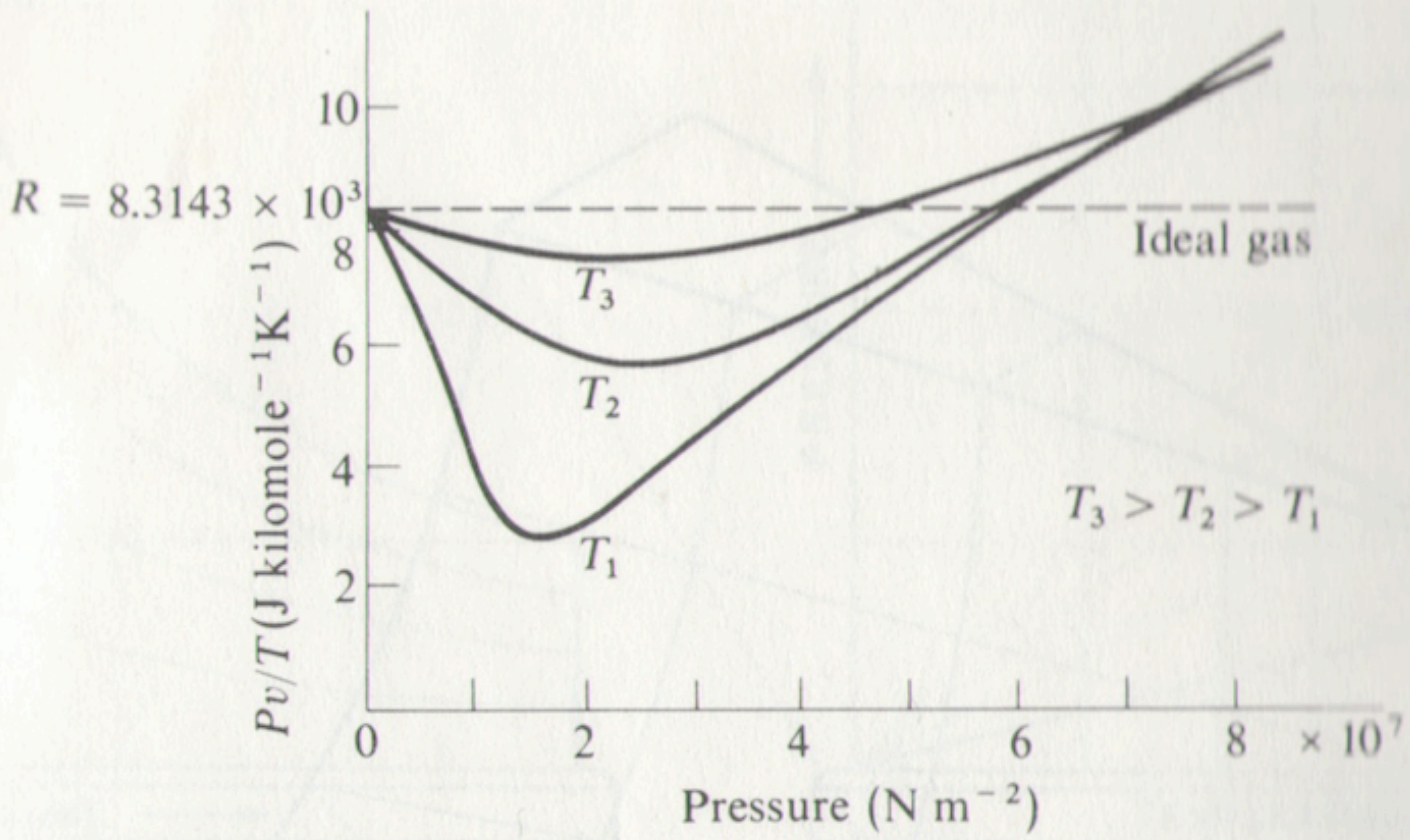


Fig. 2–1 The limiting value of Pv/T is independent of T for all gases. For an ideal gas, Pv/T is constant.

$$R = N_A k_B$$

k_B- **Boltzmann constant** $k_B \simeq 1.3807 \times 10^{-23} \frac{J}{K}$

P-v-T surface for an ideal gas

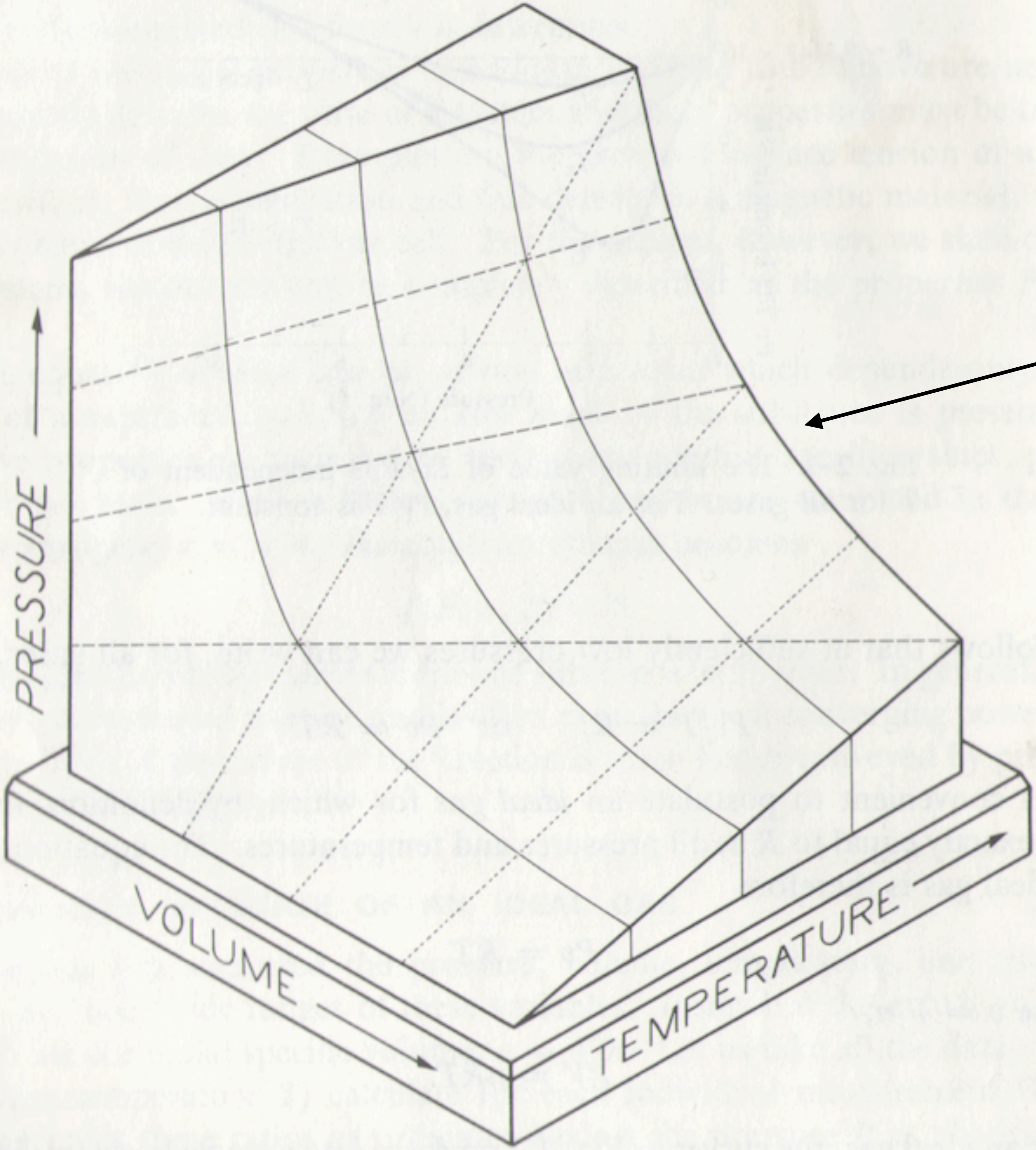
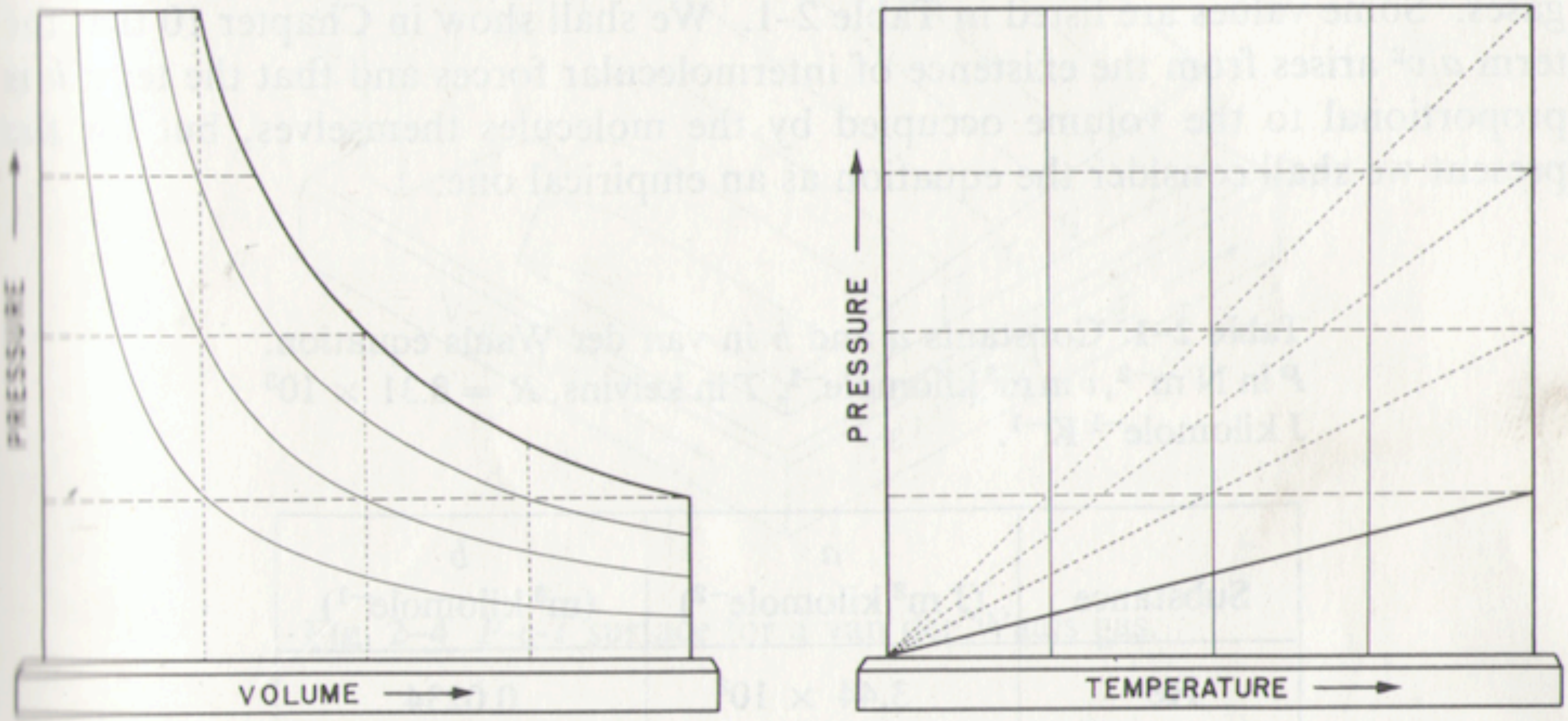


Fig. 2-2 *P-v-T* surface for an ideal gas.

$Pv = RT$



(a) (b)

Fig. 2–3 Projections of the ideal gas *P-v-T* surface onto (a) the *P-v* plane, and (b) the *P-T* plane.

Van der Waals equation for real gases

$$\left(P + \frac{a}{v^2}\right)(v - b) \ = \ RT$$

Term a/v^2 is due to intermolecular forces and term $-b$ is proportional to the volume occupied by molecules themselves

Equation of state of a real gas in the virial form

$$Pv \ = \ A + \frac{B}{v} + \frac{C}{v^2} + \ldots$$

Van der Waals equation in the virial form

$$Pv \ = \ RT + \frac{RTb - a}{v} + \frac{RTb}{v^2} + \ldots$$

P-v-T surfaces for real substances

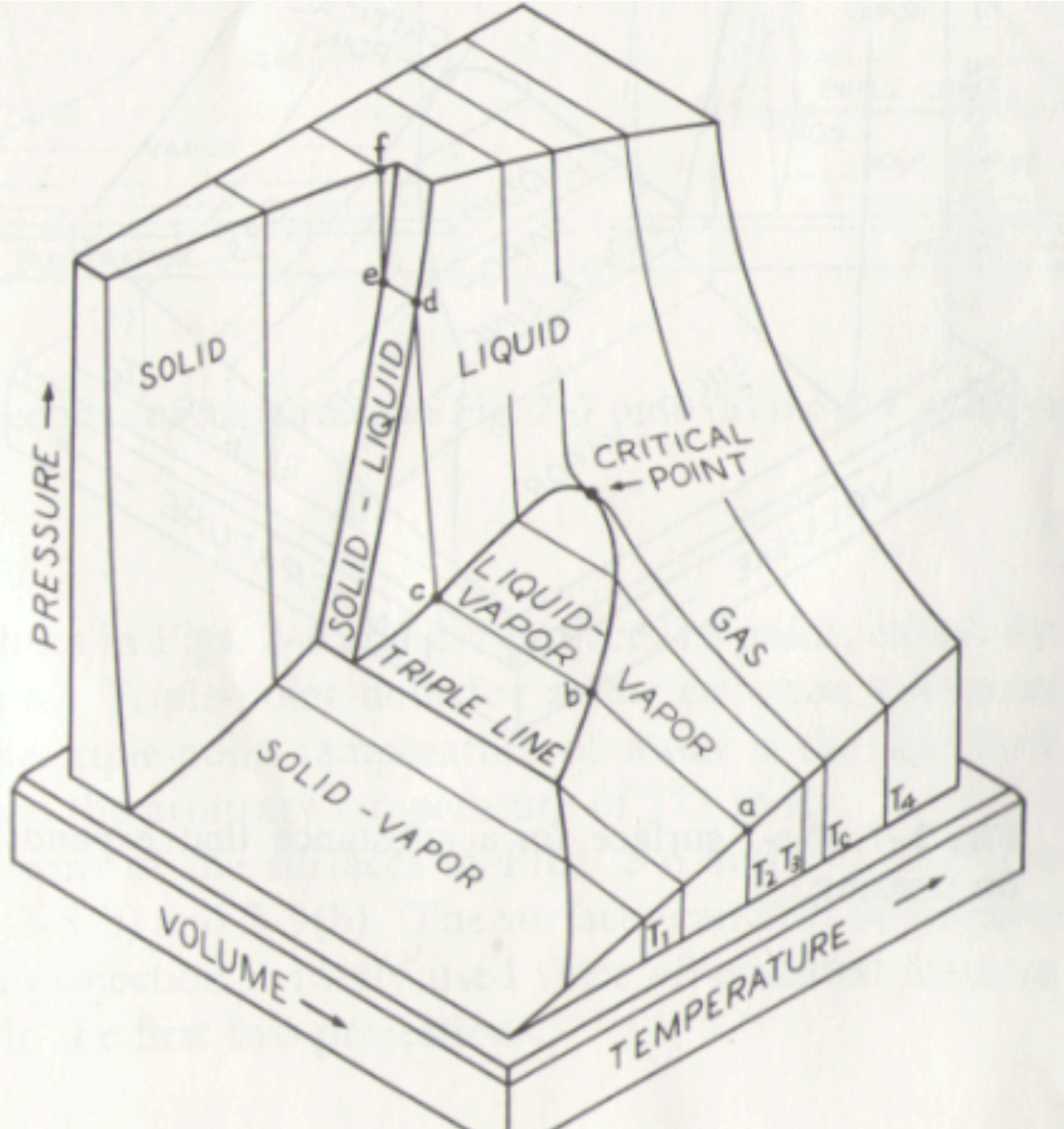
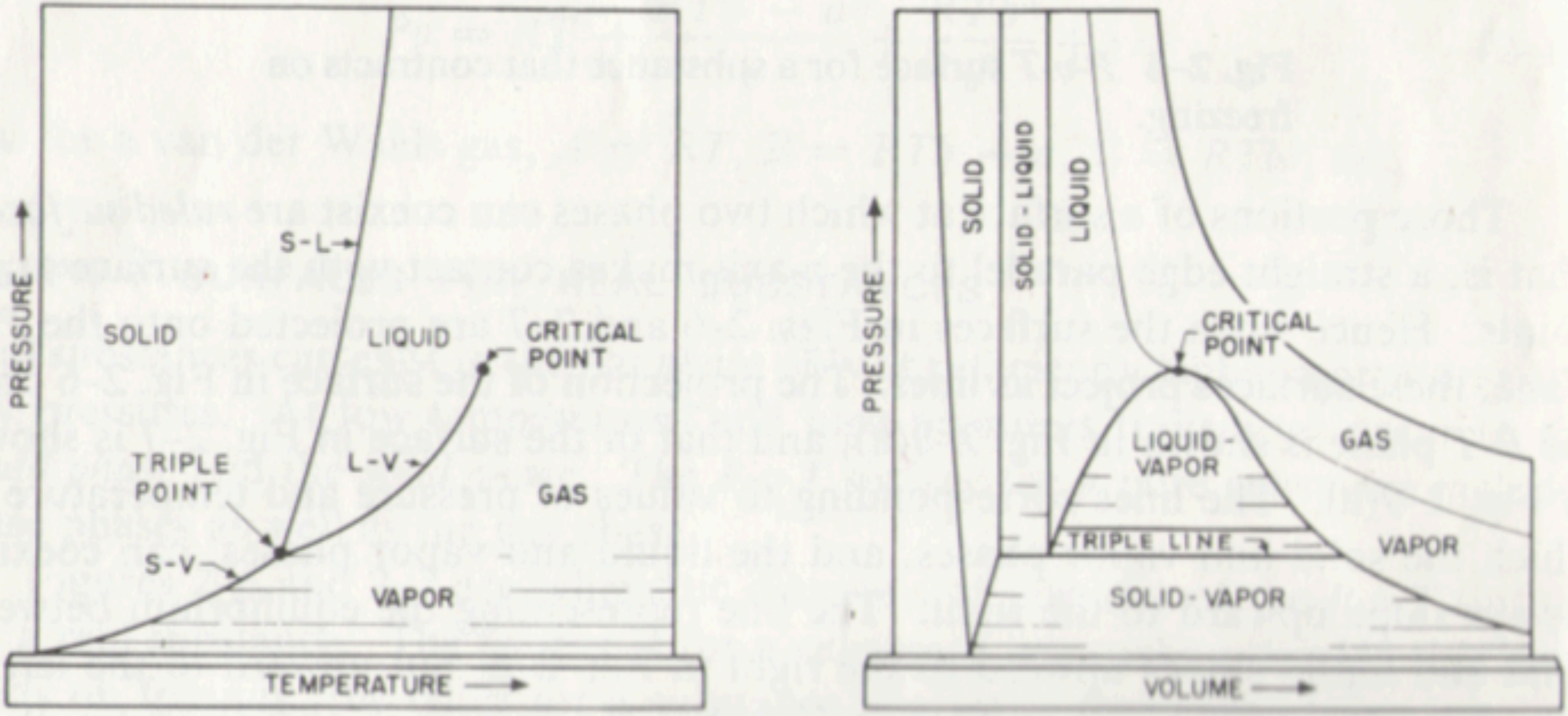


Fig. 2–6 *P-v-T* surface for a substance that contracts on freezing.

Projections



(a) (b)

Fig. 2–8 Projections of the surface in Fig. 2–6 onto (a) the *P-T* plane and (b) the *P-v* plane.

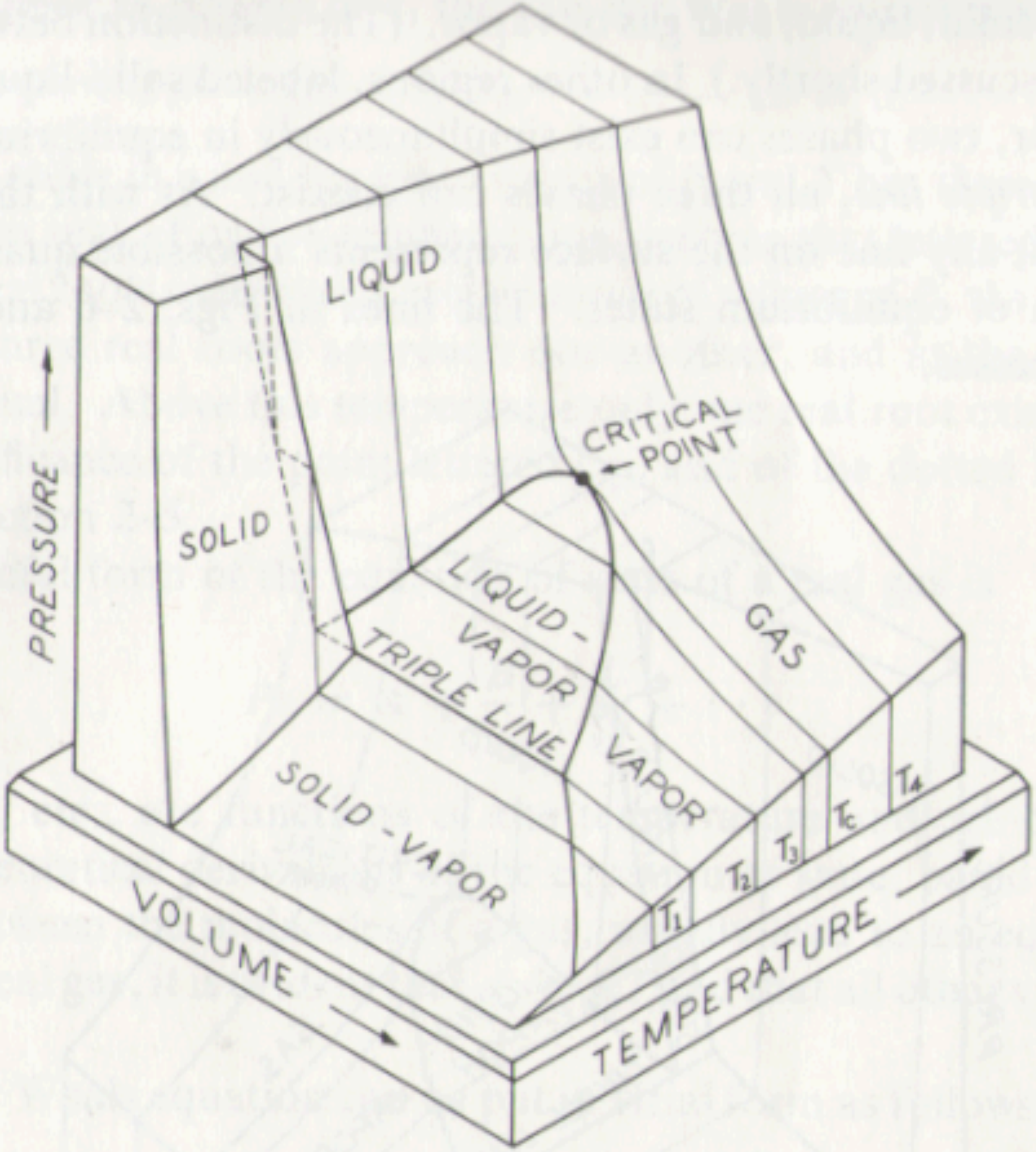


Fig. 2–7 *P-v-T* surface for a substance that expands on freezing.

Projections

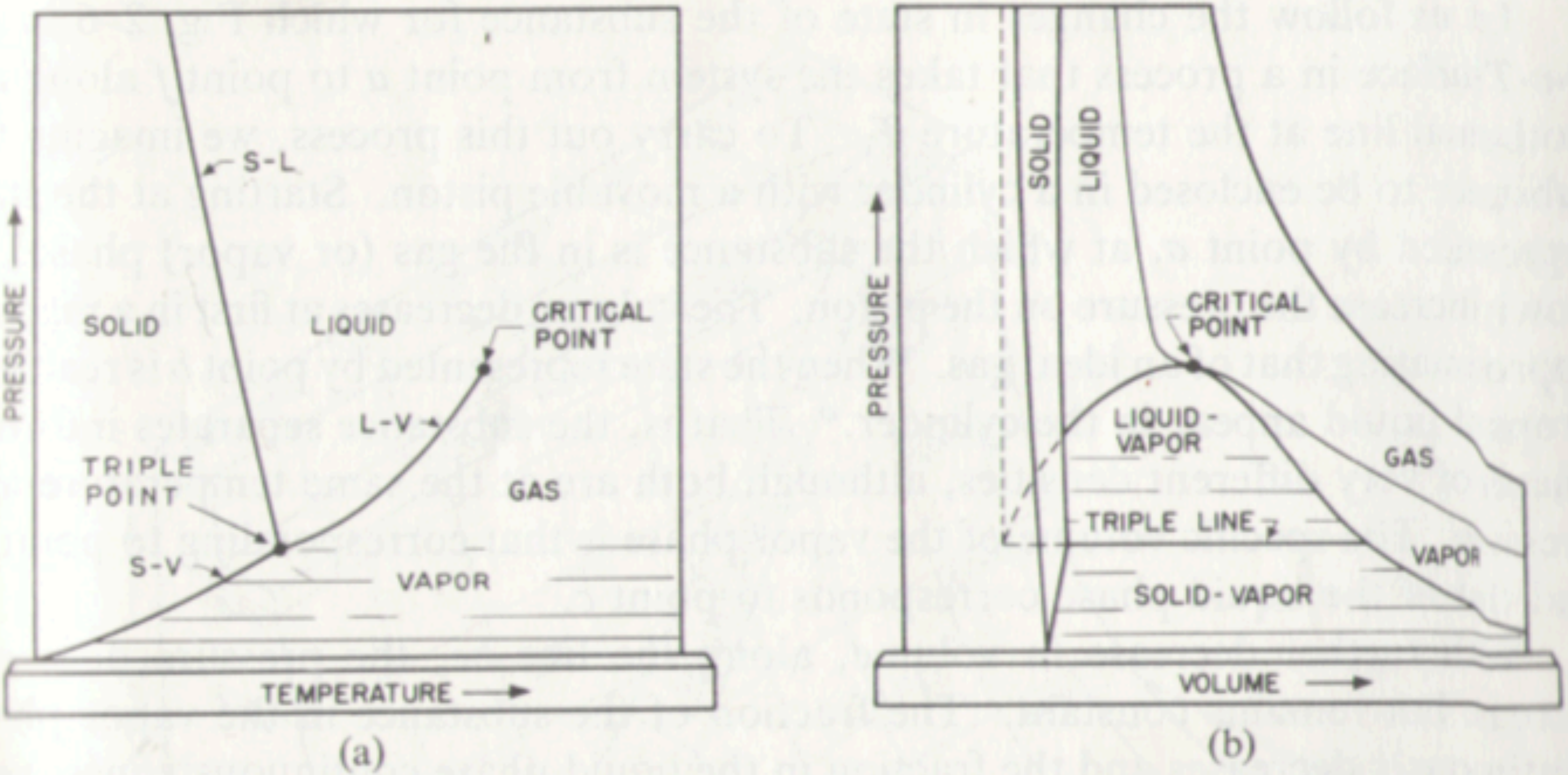
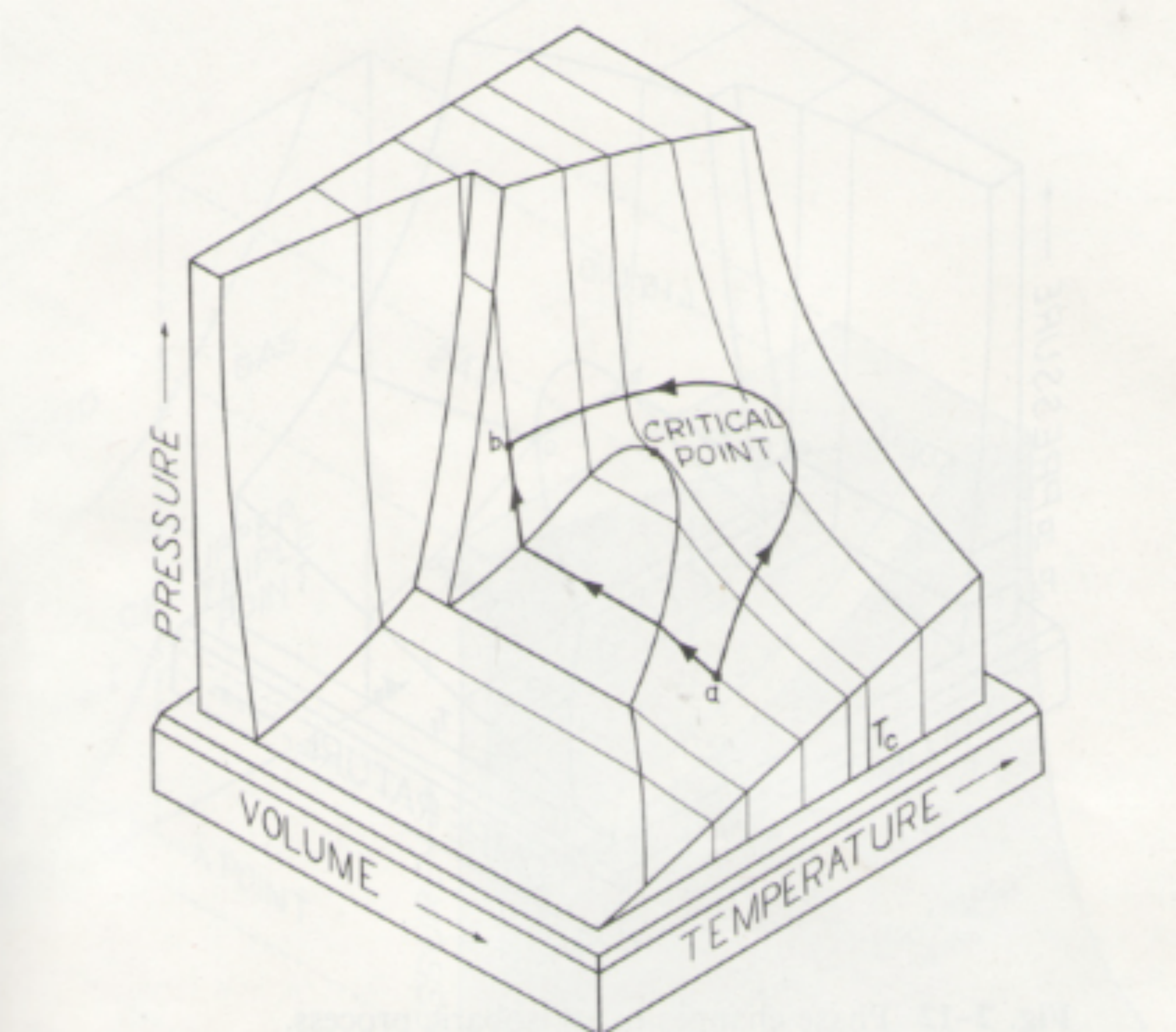


Fig. 2–9 Projections of the surface in Fig. 2–7 onto (a) the *P-T* plane and (b) the *P-v* plane.

Vapor-liquid transition around critical point



Expansivity and compressibility

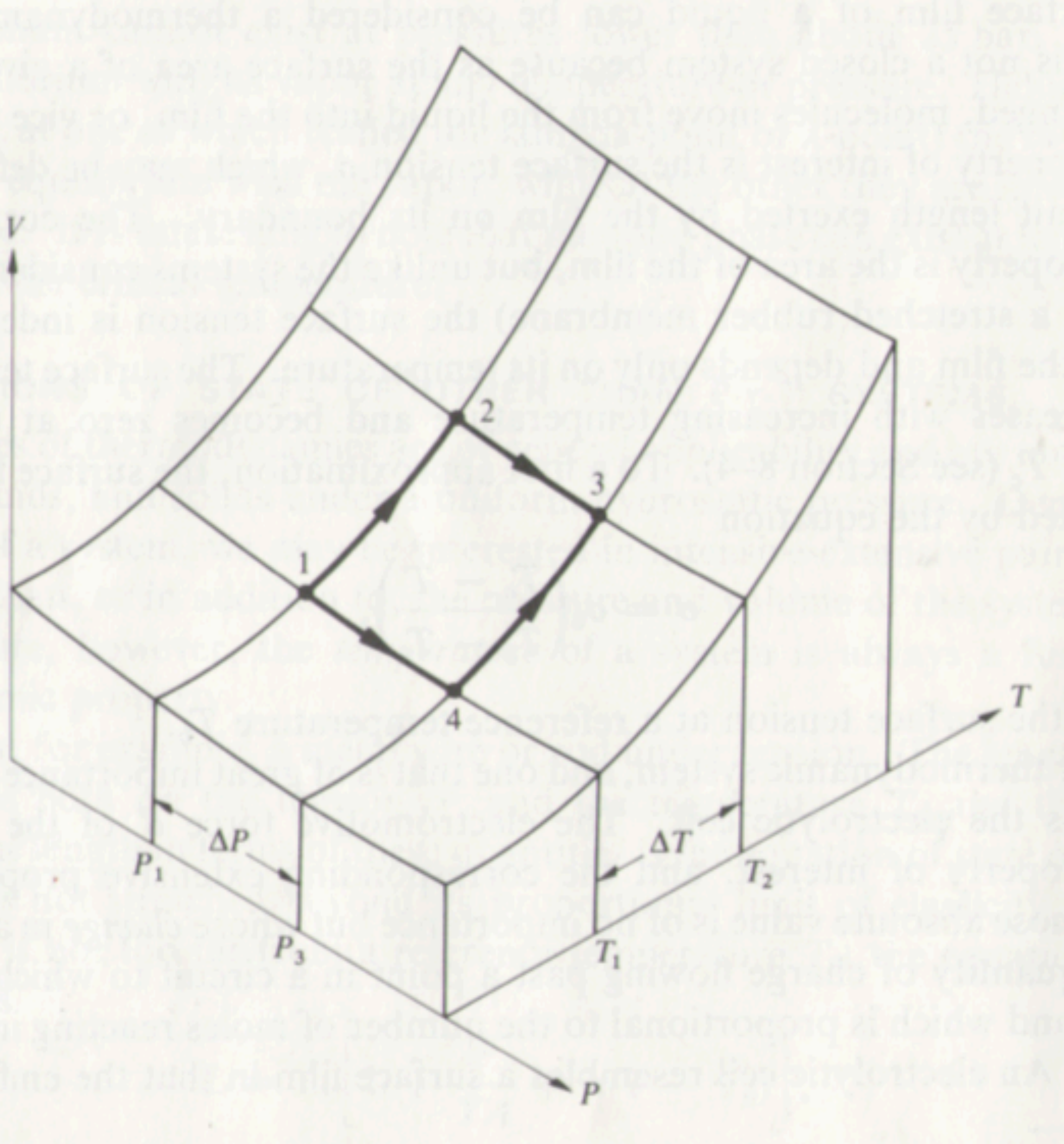


Fig. 2–14 A *P-V-T* surface for a solid or liquid. Notice that the *V* axis is now vertical and has been greatly exaggerated.

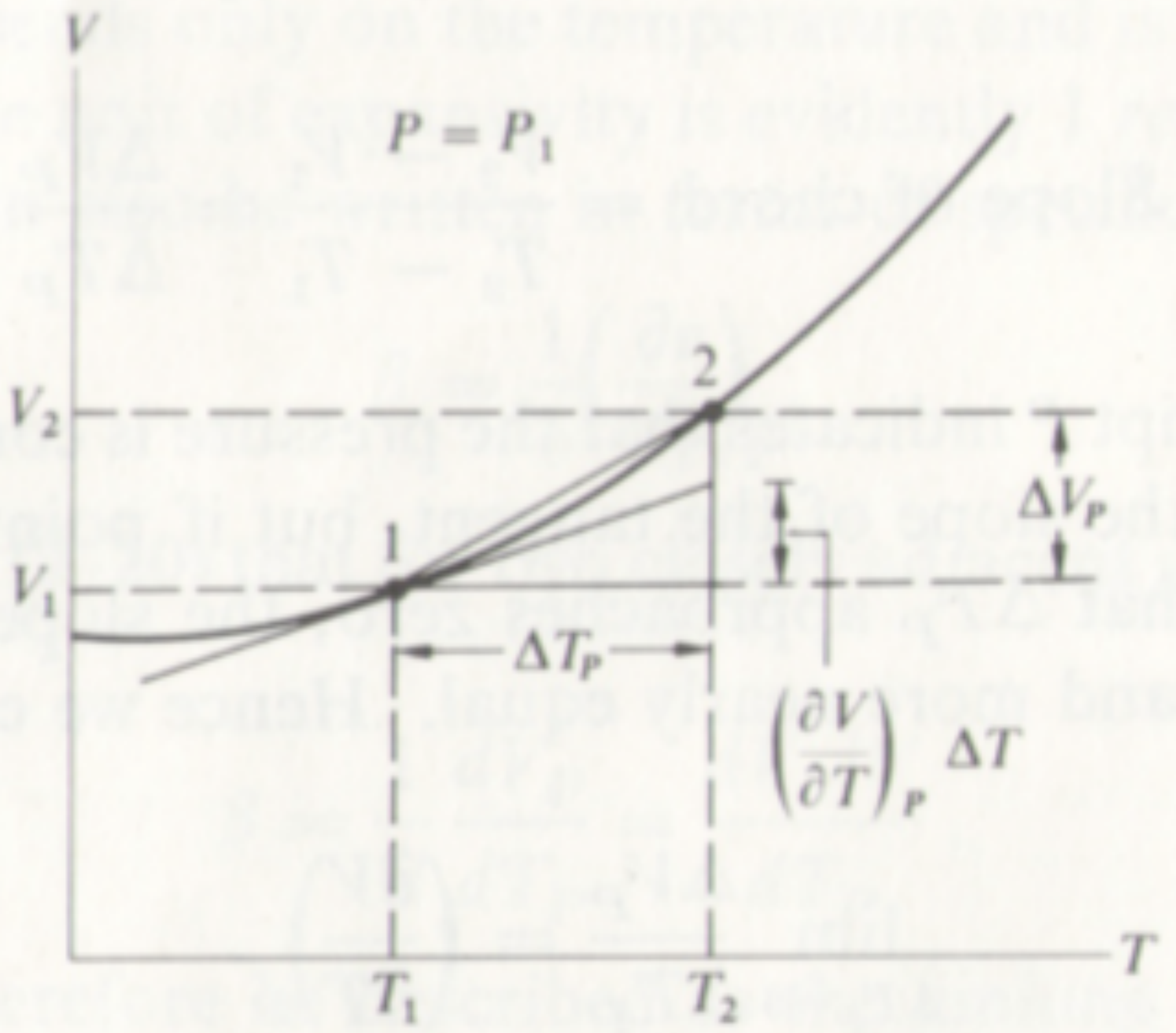


Fig. 2–15 The intersection of the surface of Fig. 2–14 with the v-T plane at pressure P_1.

$$\text{Slope of tangent} = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{Slope of chord} =$$

$$= \frac{V_2 - V_1}{T_2 - T_1} = \frac{\Delta V_P}{\Delta T_P}$$

$$\lim_{\Delta T \to 0} \Delta T \left(\frac{\partial V}{\partial T}\right)_P = \Delta V_P$$

$$\Rightarrow$$

For infinitesimal changes

$$dV_P = \left(\frac{\partial V}{\partial T}\right)_P dT_P$$

Expansivity

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

For an ideal gas $$\beta = \frac{1}{V}\frac{nR}{P} = \frac{1}{T}$$

Mean expansivity

$$\bar{\beta} = \frac{1}{V_1}\frac{V_2 - V_1}{T_2 - T_1} = \frac{1}{V_1}\frac{\Delta V_P}{\Delta T_P}$$

Compressibility

Consider an isothermal process

$$\text{Slope of tangent} = \left(\frac{\partial V}{\partial P}\right)_T$$

For infinitesimal changes $$dV_T = \left(\frac{\partial V}{\partial P}\right)_T \text{dP}$$

Compressibility

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Mean compressibility $$\bar{\kappa} = -\frac{1}{V_1}\frac{\Delta V_T}{\Delta P_T}$$

Compressibility and expansivity are functions of temperature and pressure

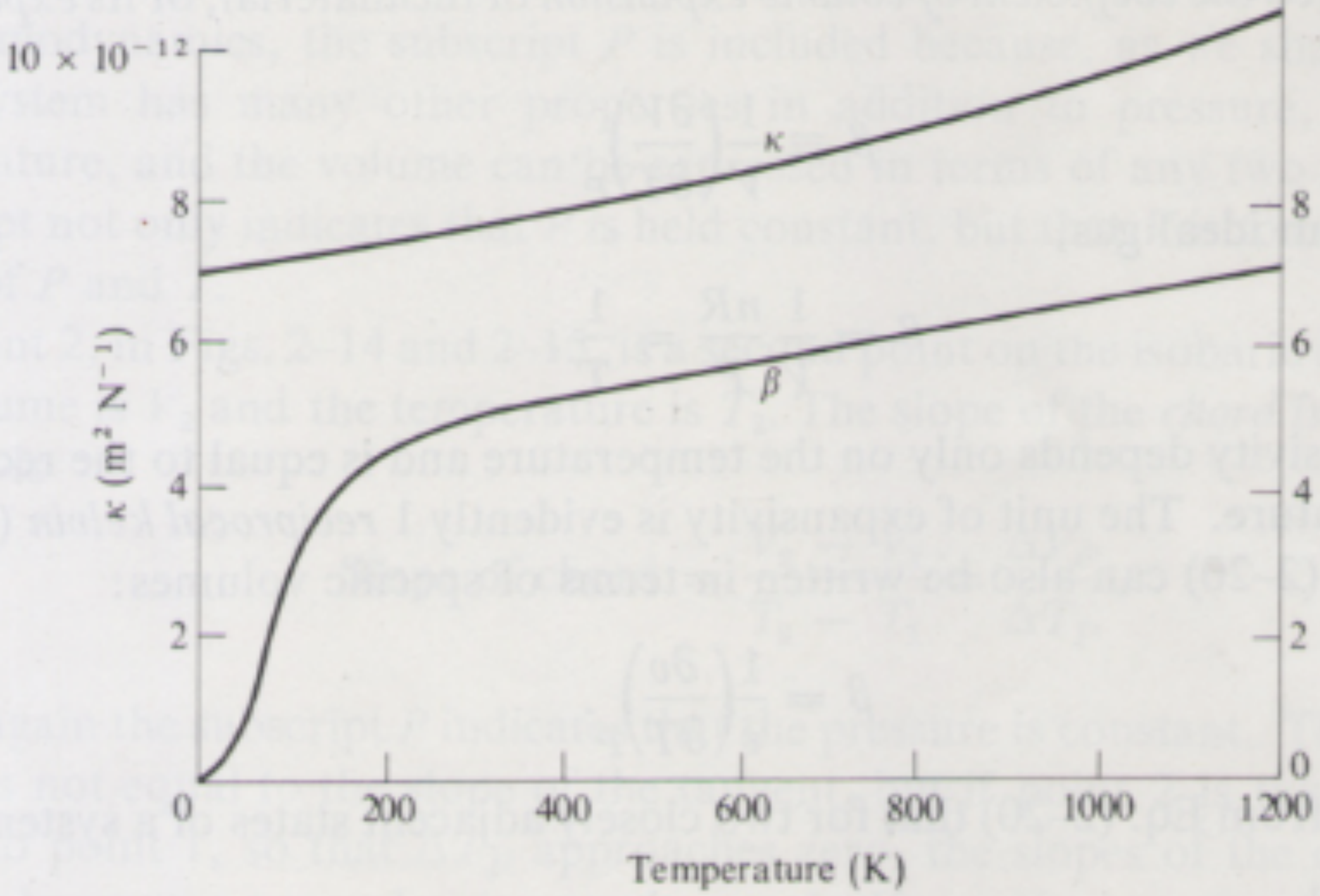


Fig. 2–16 Compressibility κ and expansivity β of copper as functions of temperature at a constant pressure of 1 atm.

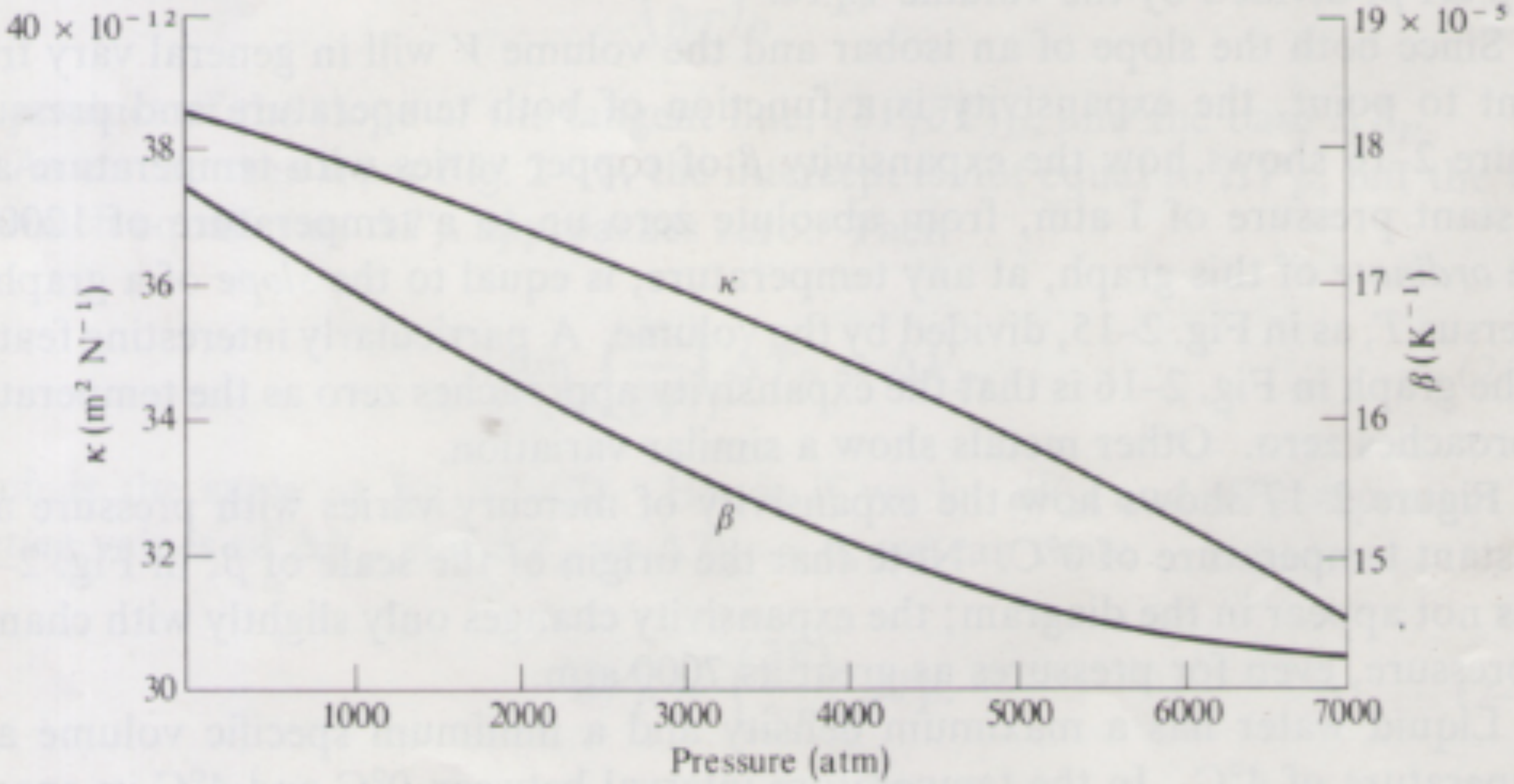


Fig. 2–17 Compressibility κ of and expansivity β of mercury as functions of pressure at a constant temperature of 0°C.

Consider an arbitrary process along the P-V-T surface

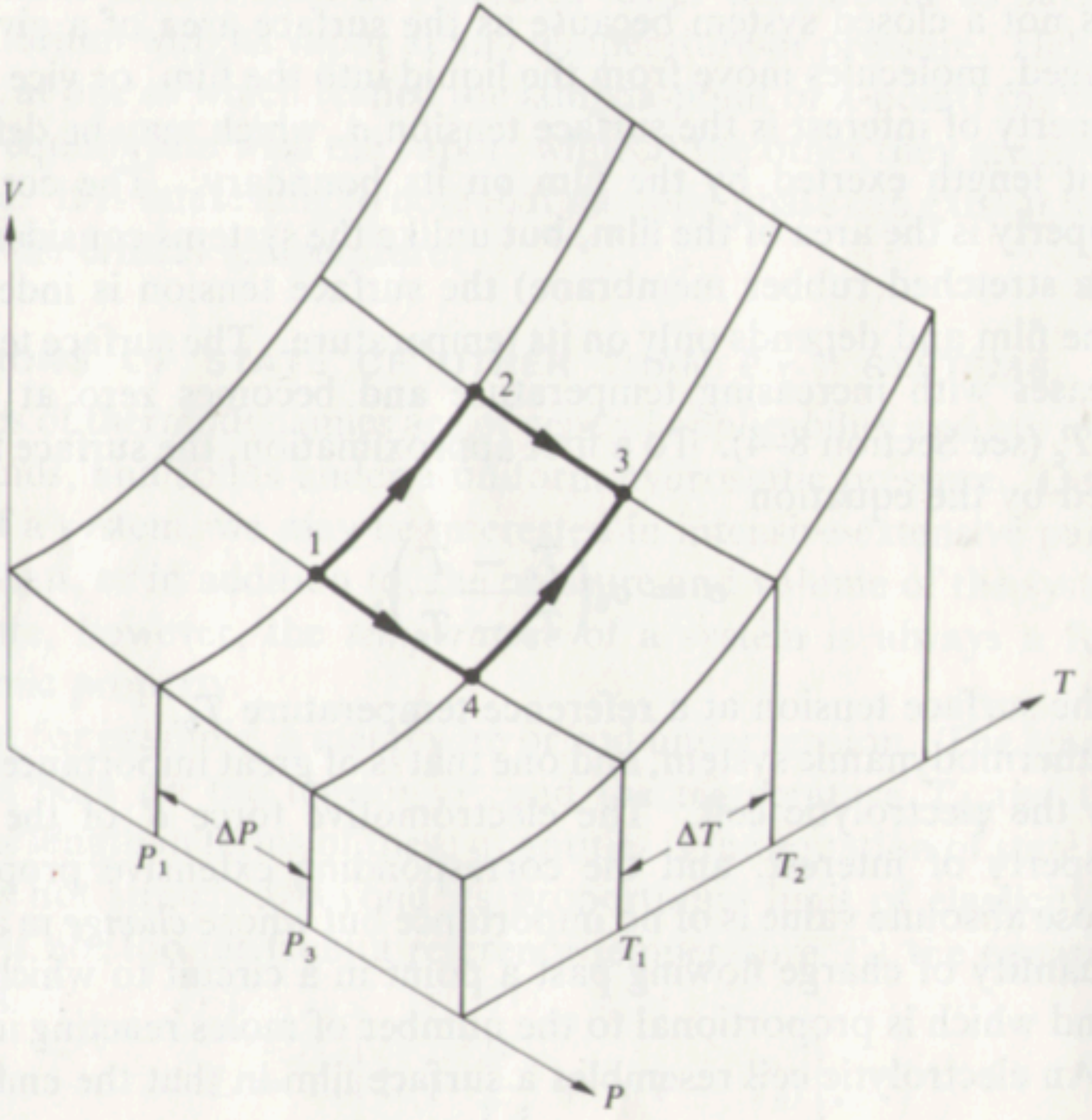


Fig. 2-14 A *P-V-T* surface for a solid or liquid. Notice that the *V* axis is now vertical and has been greatly exaggerated.

$$\Delta V(1 \to 3) \ =$$

$$= \ \Delta V_P(1 \to 2)$$

$$+ \ \Delta V_T(2 \to 3)$$

$$\Rightarrow$$

$$dV \ = \ \Big(\frac{\partial V}{\partial T}\Big)_P dT$$

$$+\Big(\frac{\partial V}{\partial P}\Big)_T dP$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial T}\right)_P dP$$

In terms of expansivity and compressibility

$$dV = \beta V dT - \kappa V dP \quad \Leftrightarrow \quad \frac{dV}{V} = \beta dT - \kappa dP$$

We can restore equation of state from expansivity and compressibility:

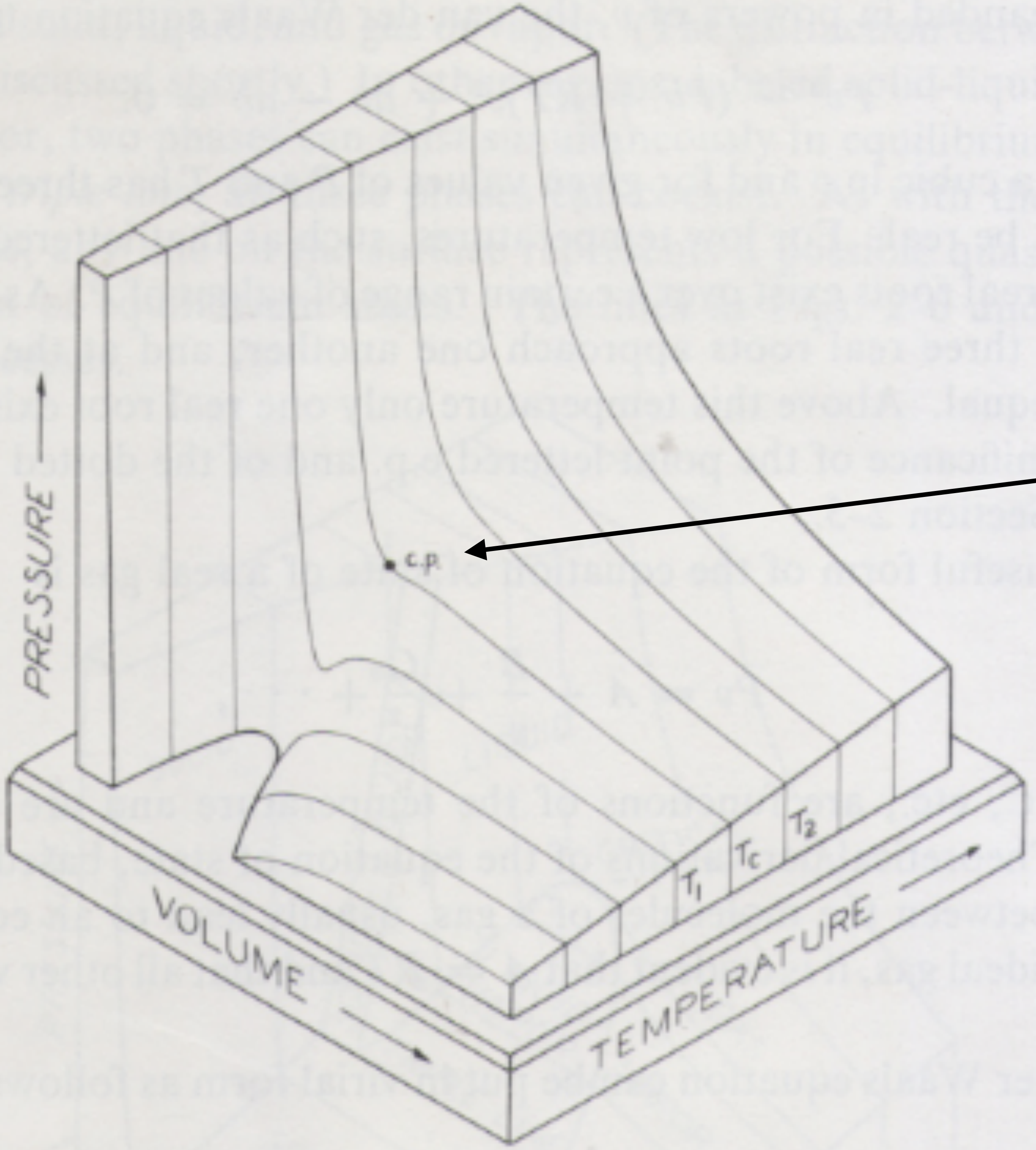
$$V - V_0 = \int_{V_0}^{V} dV = \int_{T_0}^{T} dT\, \beta V - \int_{P_0}^{P} dP\, \kappa V$$

$$\text{Ideal gas}: \ \beta = \frac{1}{T}, \ \kappa = \frac{1}{P} \ \Rightarrow \ \frac{dV}{V} - \frac{dT}{T} + \frac{dP}{P} = 0$$

$$\Rightarrow \ \ln V - \ln T + \ln P = \text{const} \ \Rightarrow \ \frac{PV}{T} = \text{const}$$

$$\text{Solid or liquid}: \ V \simeq V_0 \ \Rightarrow \ V = V_0[1 + \beta(T - T_0) - \kappa(P - P_0)]$$

Critical constants of a Van-der-Waals gas



Critical point

Fig. 2–4 *P-v-T* surface for a van der Waals gas.

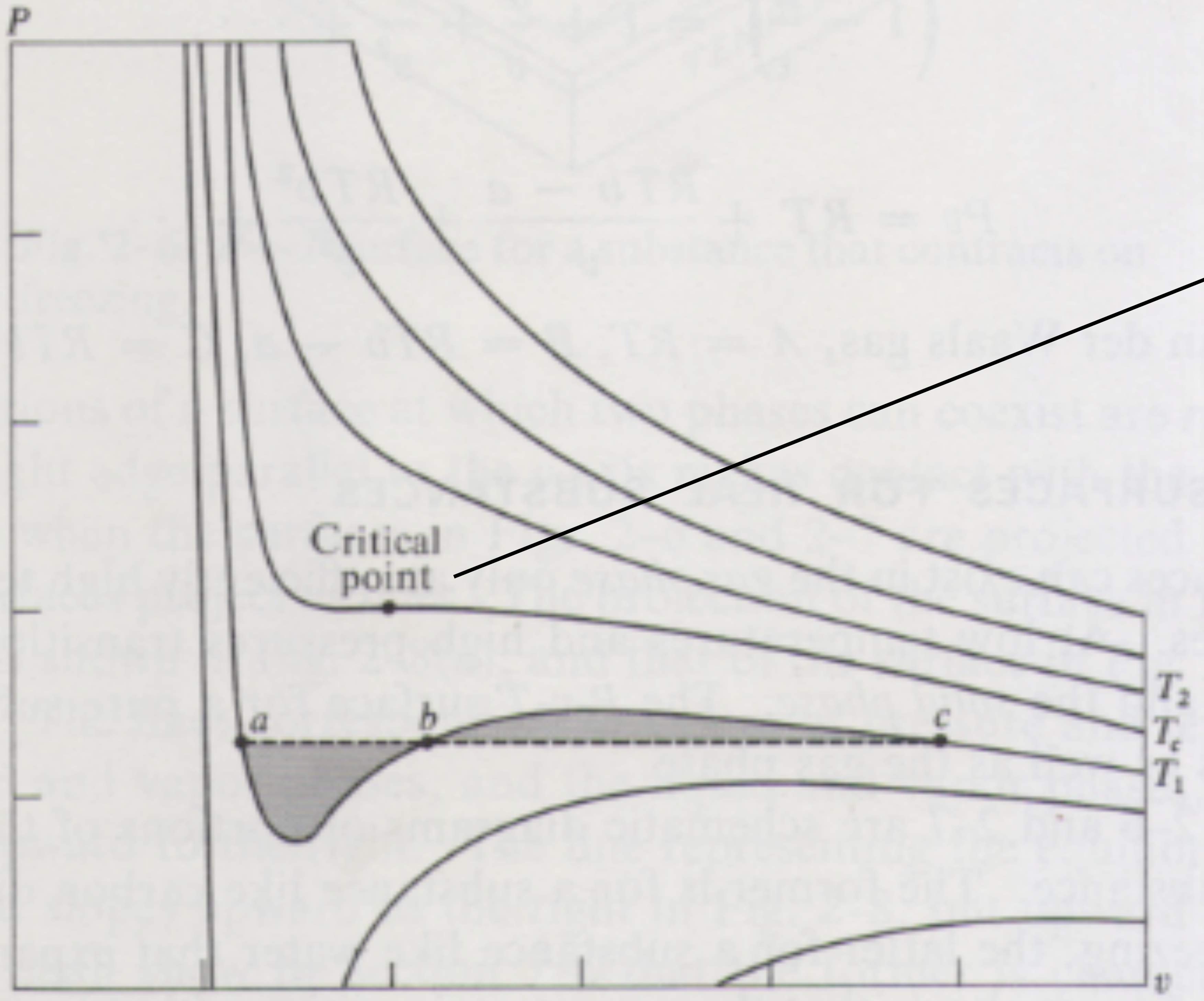


Fig. 2–5 Isotherms of a van der Waals gas.

$$\left(\frac{\partial P}{\partial v}\right)_T = 0,$$
$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$$

For a Van der Waals gas

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \Rightarrow \quad \begin{aligned} \left(\frac{\partial P}{\partial v}\right)_T &= -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}, \\ \left(\frac{\partial^2 P}{\partial v^2}\right)_T &= \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} \end{aligned}$$

$$\text{When} \quad T = T_c \quad \text{and} \quad v = v_c \qquad \left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$$

$$\Rightarrow \quad P_c = \frac{a}{27b^2}, \quad v_c = 3b, \quad T_c = \frac{8a}{27Rb}$$

$$\Rightarrow \quad \frac{P_c v_c}{T_c} = \frac{3}{8} = 0.375$$

$$\left.\frac{P_c v_c}{T_c}\right|_{\text{VdW gas}} = 0.375$$

Compare to real gases

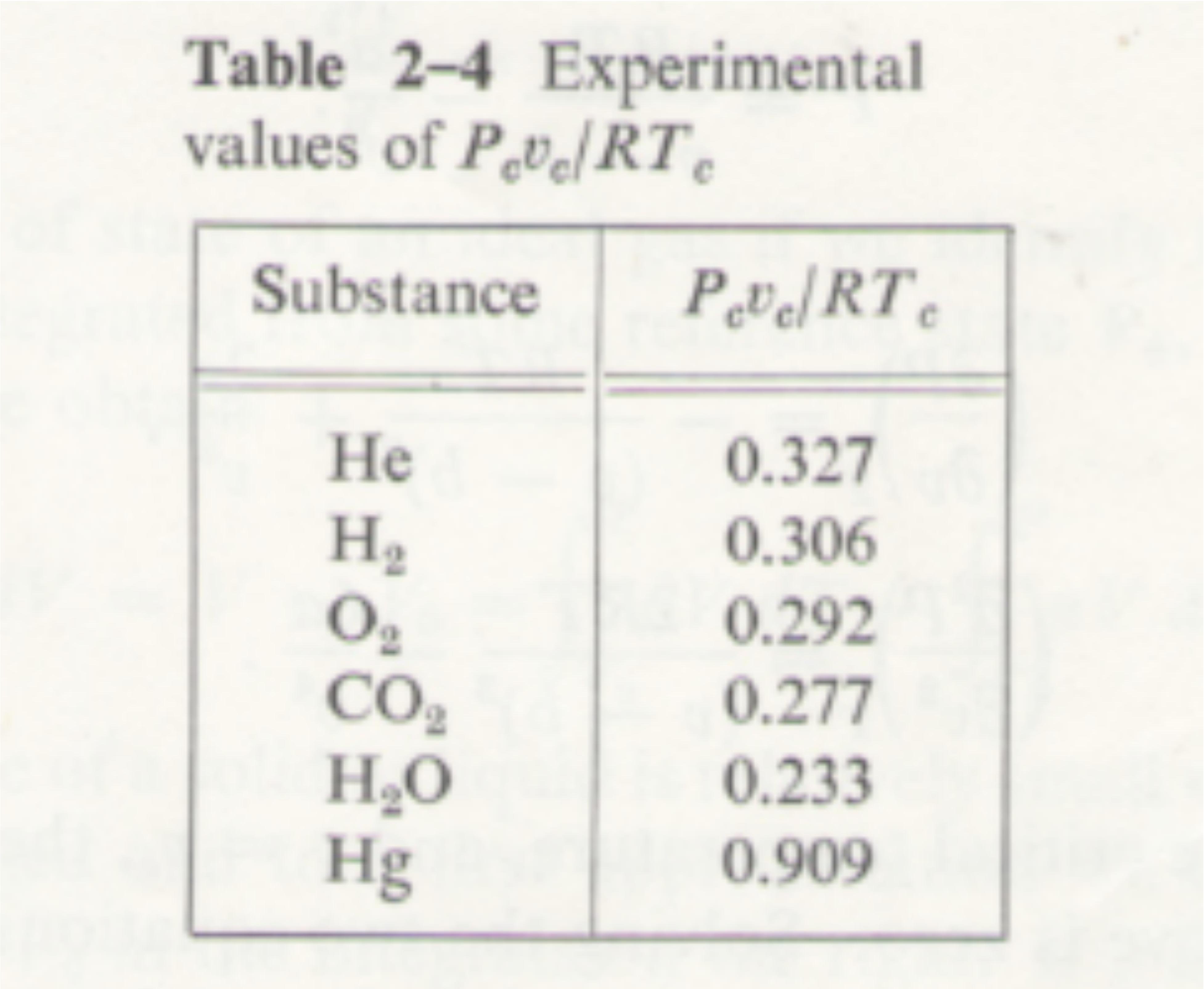


Table 2–4 Experimental values of $P_c v_c / RT_c$

Substance	$P_c v_c / RT_c$
He	0.327
H_2	0.306
O_2	0.292
CO_2	0.277
H_2O	0.233
Hg	0.909

Relations between partial derivatives

$$V = V(P,T) \quad \Rightarrow \quad dV \;=\; \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP,$$

$$P = P(V,T) \quad \Rightarrow \quad dP \;=\; \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$\Rightarrow \quad \left[1 - \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T\right] dV \;=\; \left[\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P\right] dT$$

Take $dT = 0$

$$\Rightarrow \quad 1 - \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T \;=\; 0 \quad \Leftrightarrow \quad \left(\frac{\partial V}{\partial P}\right)_T \;=\; \frac{1}{(\partial P/\partial V})_T$$

Take $dP = 0$ $\quad \Rightarrow \quad \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P \;=\; 0$

$$\left(\frac{\partial V}{\partial T}\right)_P \;=\; \frac{1}{(\partial T/\partial V)_P} \qquad \Rightarrow \quad \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \;=\; -1$$

Mathematically

$$f(x,y,z) = 0 \quad \Rightarrow$$

$$\frac{df[x,y,z(x,y)]}{dx} = \frac{\partial f[x,y,z(x,y)]}{\partial x} + \frac{\partial f[x,y,z(x,y)]}{\partial z}\frac{\partial z(x,y)}{\partial x} = 0$$

$$\Rightarrow \frac{\partial z(x,y)}{\partial x} = -\frac{\frac{\partial f[x,y,z]}{\partial x}}{\frac{\partial f[x,y,z]}{\partial z}}$$

Cyclic permutations x -> y -> z -> x

$$\frac{\partial z(x,y)}{\partial x}\frac{\partial x(y,z)}{\partial y}\frac{\partial y(z,x)}{\partial z} =$$

$$= -\frac{\frac{\partial f[x,y,z]}{\partial x}}{\frac{\partial f[x,y,z]}{\partial z}}\frac{\frac{\partial f[x,y,z]}{\partial y}}{\frac{\partial f[x,y,z]}{\partial x}}\frac{\frac{\partial f[x,y,z]}{\partial z}}{\frac{\partial f[x,y,z]}{\partial y}} = -1$$

$$\frac{df[x,y,z(x,y)]}{dx} = \frac{\partial f[x,y,z(x,y)]}{\partial x} + \frac{\partial f[x,y,z(x,y)]}{\partial z}\frac{\partial z(x,y)}{\partial x} = 0$$

$$\Rightarrow \frac{\partial z(x,y)}{\partial x} = -\frac{\frac{\partial f[x,y,z]}{\partial x}}{\frac{\partial f[x,y,z]}{\partial z}}$$

$$\frac{df[x(y,z),y,z]}{dz} = \frac{\partial f[x(y,z),y,z]}{\partial z} + \frac{\partial f[x(y,z),y,z]}{\partial x}\frac{\partial x(y,z)}{\partial z} = 0$$

$$\Rightarrow \frac{\partial x(y,z)}{\partial z} = -\frac{\frac{\partial f[x,y,z]}{\partial z}}{\frac{\partial f[x,y,z]}{\partial x}}$$

$$\Rightarrow \frac{\partial x(y,z)}{\partial z}\frac{\partial z(x,y)}{\partial x} = 1$$

Expansivity and compressibility

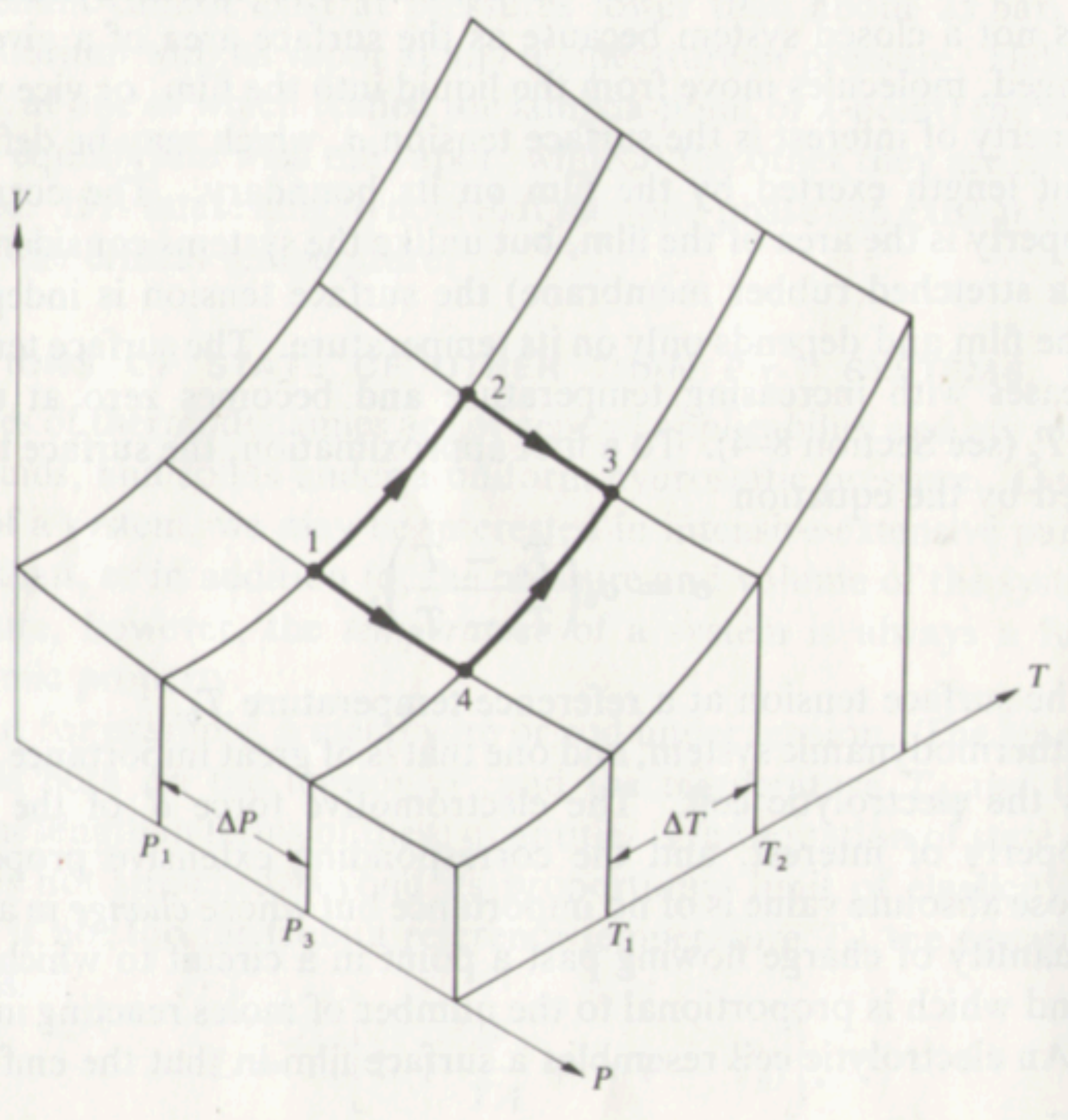


Fig. 2–14 A *P-V-T* surface for a solid or liquid. Notice that the *V* axis is now vertical and has been greatly exaggerated.

Exact differentials

Along path 1->2->3 $\quad dV_{1\rightarrow 2\rightarrow 3} = \left(\frac{\partial V}{\partial T}\right)_{P_1} dT + \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$

Along path 1->4->3 $\quad dV_{1\rightarrow 4\rightarrow 3} = \left(\frac{\partial V}{\partial P}\right)_{T_1} dP + \left(\frac{\partial V}{\partial T}\right)_{P_3} dT$

$$\Rightarrow \left(\frac{\partial V}{\partial P}\right)_{T_1} dP + \left(\frac{\partial V}{\partial T}\right)_{P_3} dT = \left(\frac{\partial V}{\partial P}\right)_{T_2} dP + \left(\frac{\partial V}{\partial T}\right)_{P_1} dT$$

Since $\quad T_2 = T_1 + dT \text{ and } P_3 = P_1 + dP$

$$\Rightarrow \frac{\left(\frac{\partial V}{\partial T}\right)_{P_1} - \left(\frac{\partial V}{\partial T}\right)_{P_1+dP}}{dP} = \frac{\left(\frac{\partial V}{\partial P}\right)_{T_1} - \left(\frac{\partial V}{\partial P}\right)_{T_1+dT}}{dT}$$

$$\Rightarrow \frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right) \equiv \frac{\partial^2 V}{\partial P \partial T}$$

$$dV = (\frac{\partial V}{\partial T}\Big)_P dT + \Big(\frac{\partial V}{\partial P}\Big)_T dP$$ is an exact differential

Definition: the differential $g(x,y)dx + h(x,y)dy$

is called an exact differential if $$\frac{\partial g(x,y)}{\partial y} = \frac{\partial h(x,y)}{\partial x} \; .$$

Indeed, if $g(x,y)\,dx + h(x,y)\,dy \;=\; df(x,y)$

$$g(x,y) \;=\; \frac{\partial f(x,y)}{\partial x}, \quad h(x,y) \;=\; \frac{\partial f(x,y)}{\partial y} \quad \Rightarrow \quad \frac{\partial g(x,y)}{\partial y} \;=\; \frac{\partial h(x,y)}{\partial x} \;=\; \frac{\partial^2 f(x,y)}{\partial x \partial y}$$

Integral of exact differential between two points in the (x,y) plane does not depend on the form of the path in the (x,y) plane:

$$\int_{(x_1,y_1)}^{(x_2,y_2)} \big[g(x,y)\,dx + h(x,y)\,dy\big] \;=\; f(x_2,y_2) - f(x_1,y_1)$$

Work in a volume change

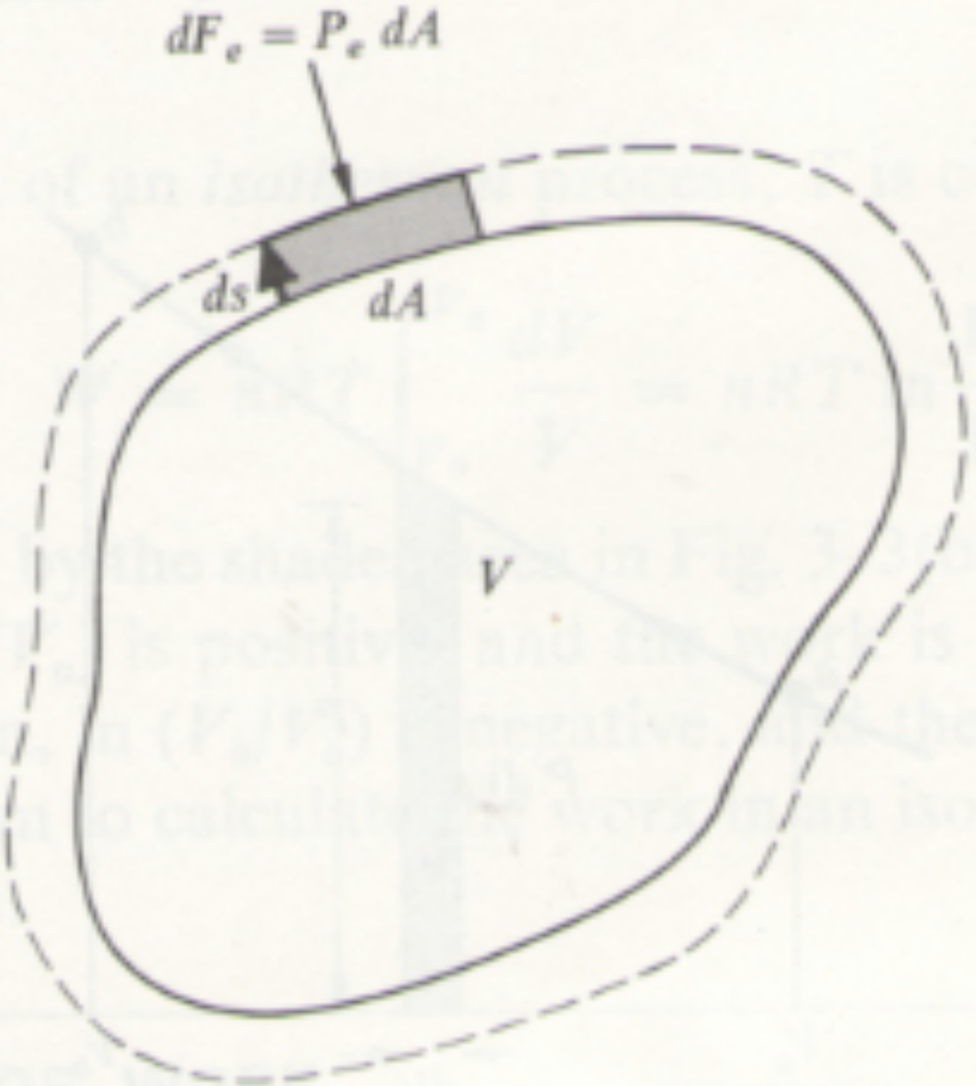


Fig. 3–1 The work done by a system expanding against an external force is given by $P_e\,dA\,ds$.

$$dF = P_{\text{ext}} dA$$

$$\Rightarrow dW = dF ds$$

$$= P_{\text{ext}} dA ds \;\equiv P_{\text{ext}} dV$$

In thermodynamics dW is positive when the work is done by the system

If the process is reversible $P_{\text{ext}} = P$ and

$$dW \;=\; PdV \;\Rightarrow$$

$$W \;=\; \int_{V_a}^{V_b} PdV$$

On a P-V diagram

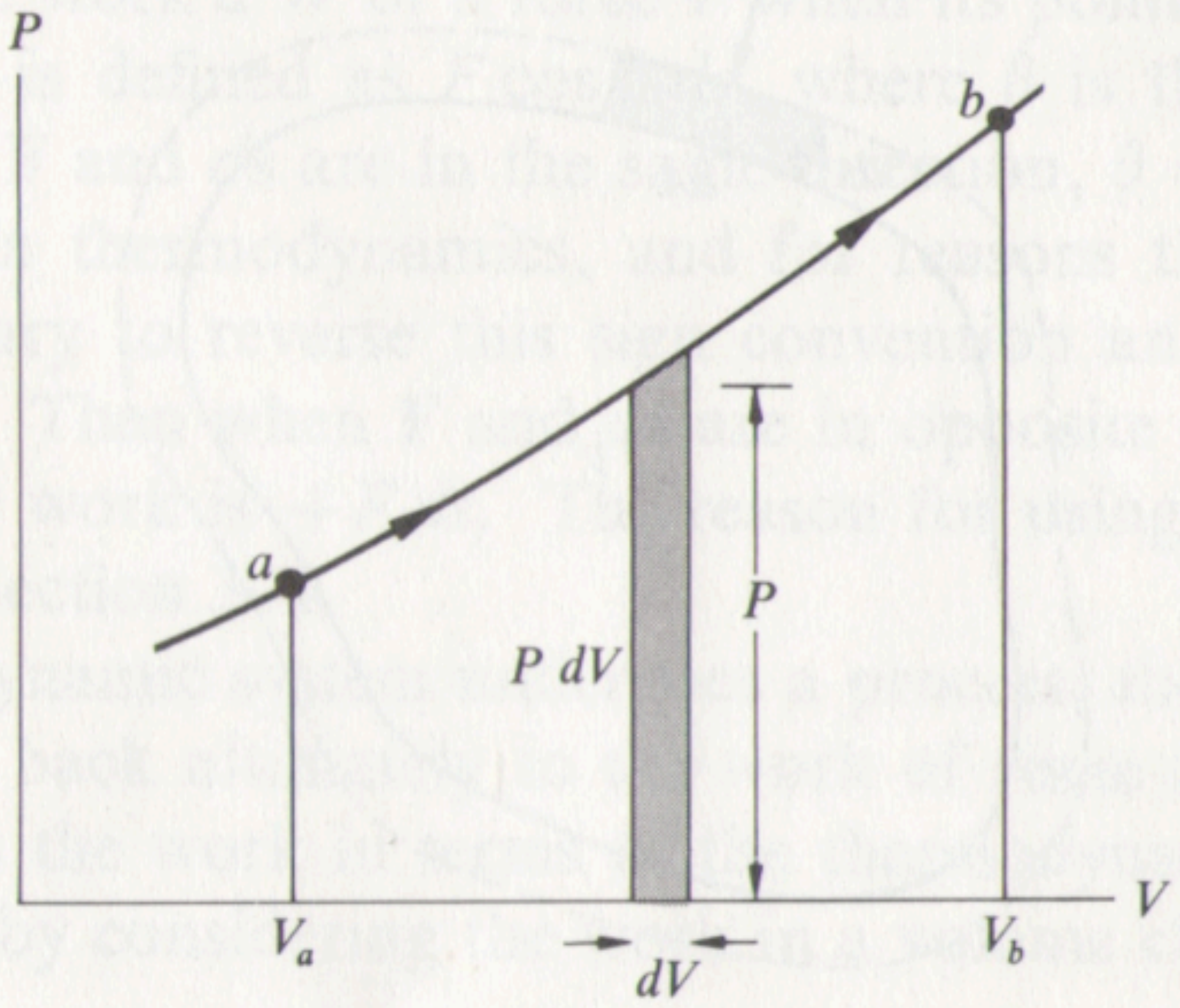


Fig. 3–2 The shaded area represents the work in a small volume change.

$$
\begin{aligned}
dW &= PdV \Rightarrow \\
W &= \int_{V_a}^{V_b} PdV
\end{aligned}
$$

Isobaric **Isothermal**

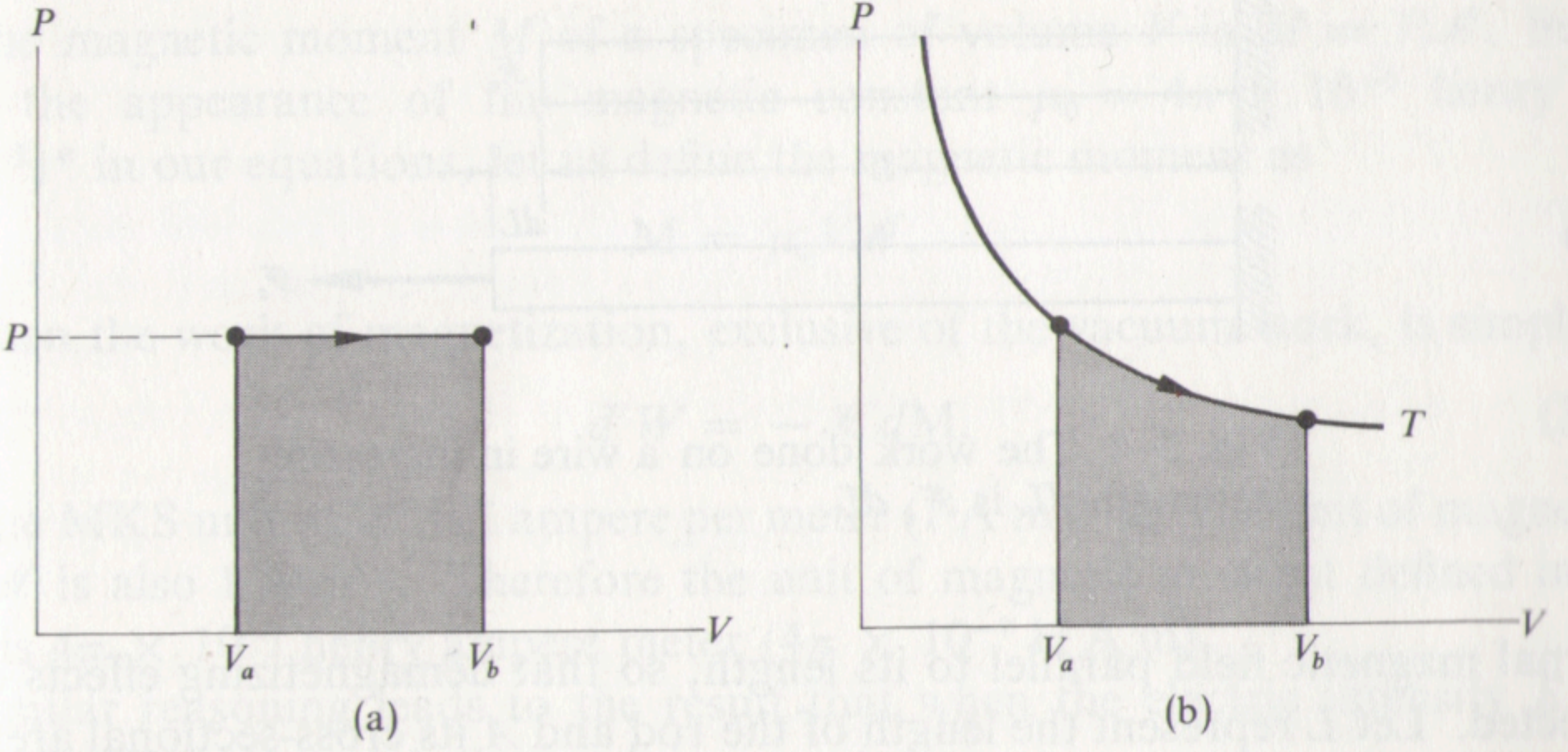


Fig. 3–3 The shaded area represents the work in an (a) isobaric process, (b) isothermal process.

$$W = P(V_b - V_a)$$

$$W = \int_{V_a}^{V_b} P dV \;=\; nRT \ln \frac{V_b}{V_a}$$

Other forms of work

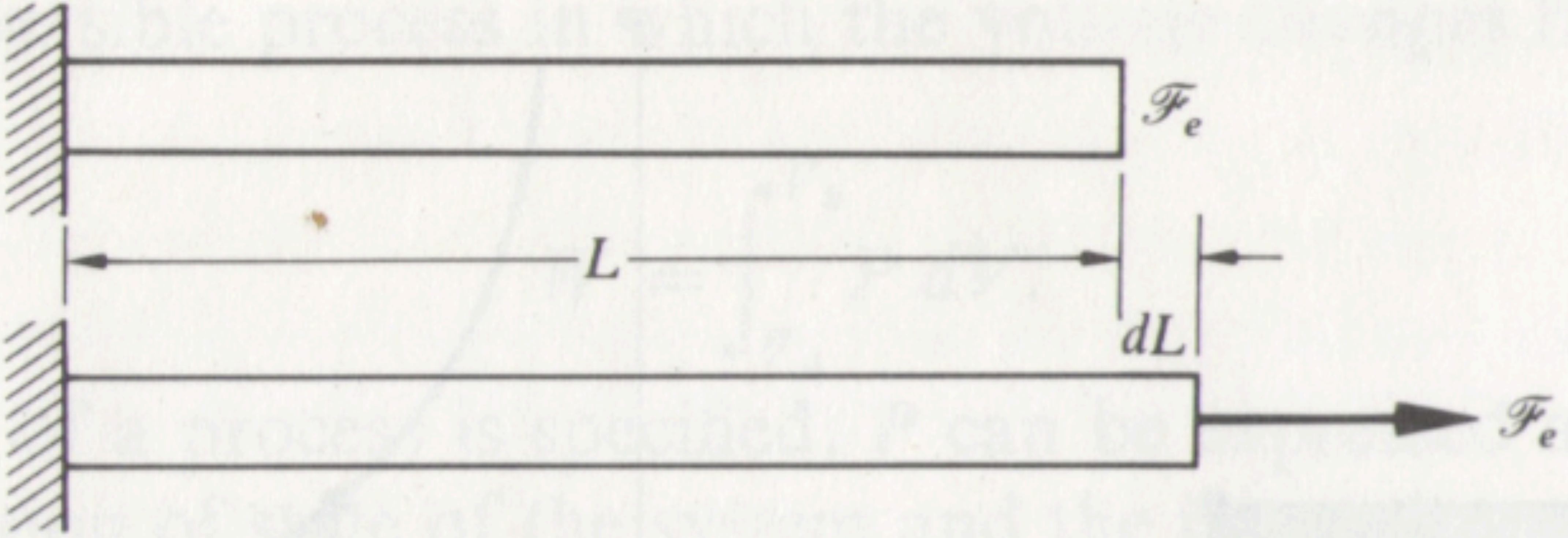
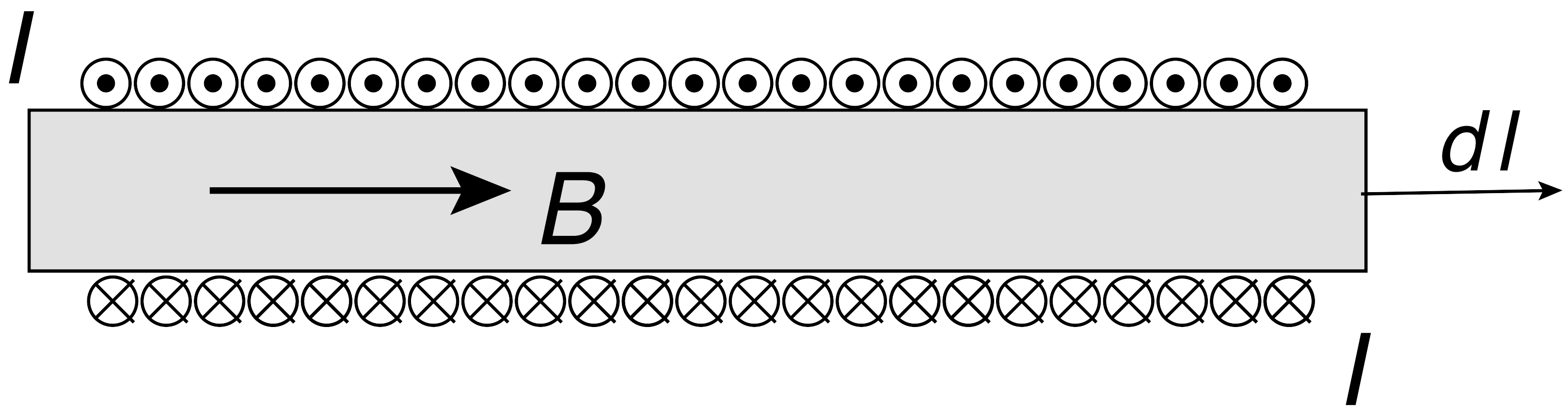


Fig. 3–4 The work done on a wire in increasing its length dL is $\mathscr{F}_e\, dL$.

$$dW = -\mathcal{F}_{\text{ext}} dl = -\mathcal{F} dl$$

Work *vs* change in magnetization



$$\mathcal{E} = -N\frac{d\phi}{dt} = -NA\frac{dB}{dt} \qquad \mathcal{P} = \mathcal{E}I \;\Rightarrow\; dW = \mathcal{P}dt = \mathcal{E}Idt$$

$$H = \frac{NI}{L} \;\rightarrow\; dW = VHdB, \qquad V \equiv AL$$

Magnetization $\mathcal{M}$ = magnetic moment per unit volume

$$B = \mu_0(H + \mathcal{M}) \;\Rightarrow\; dW = -\mu_0 VHdH - \mu_0 VHd\mathcal{M}$$

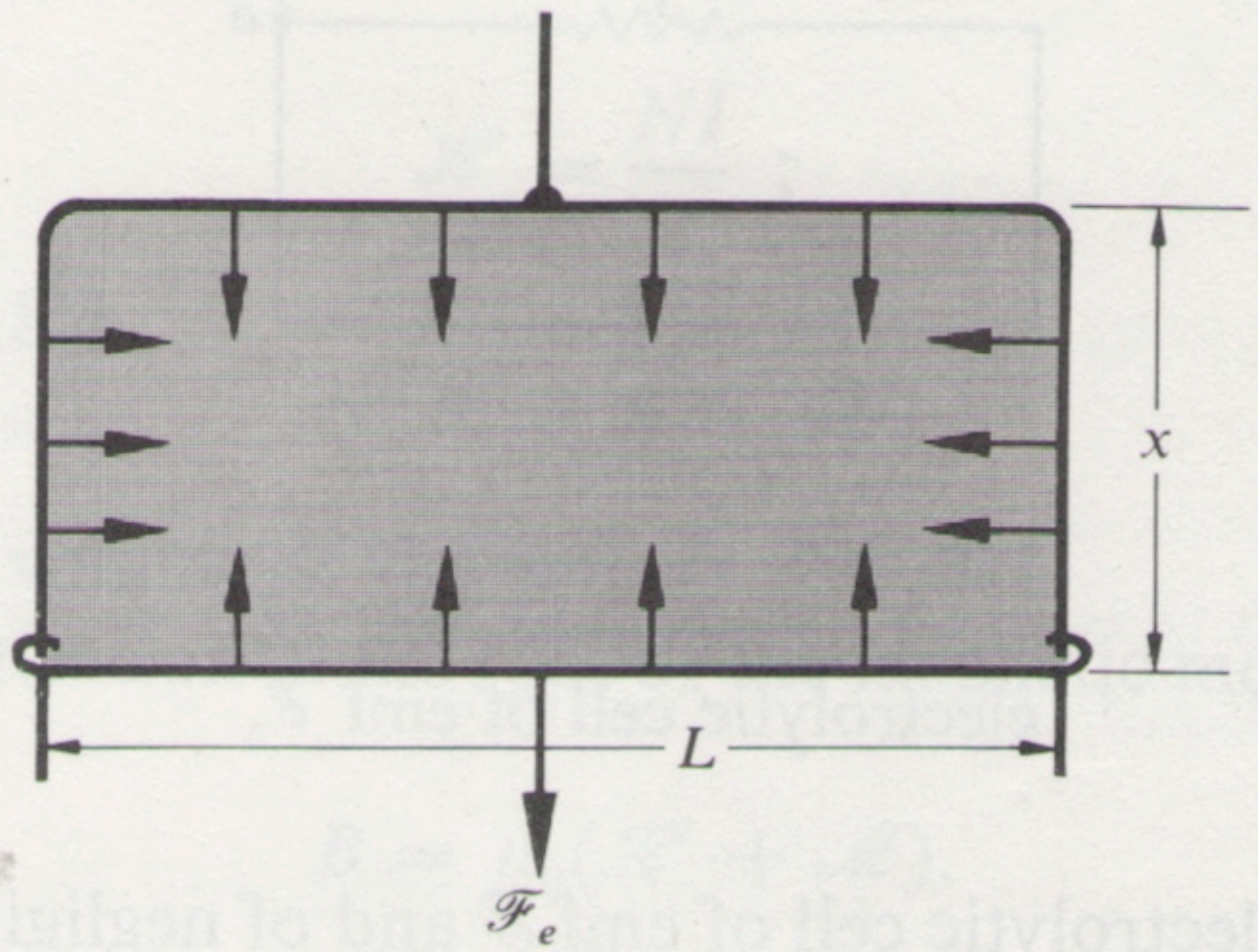
The second term is the work due to the change of magnetization of the rod

Define $M \equiv \mu_0 V\mathcal{M}$

$\Rightarrow$ The work of magnetization is

$$dW_{\mathrm{mag}} = -HdM$$

Surface tension $\sigma \equiv$ inward force exerted by film surface per unit length of boundary



$$dW = -F_{\text{ext}} dx = -2\sigma L dx = -\sigma dA$$

Work is not a property of the system

dW is not an exact differential $\Rightarrow$ we will denote it δW

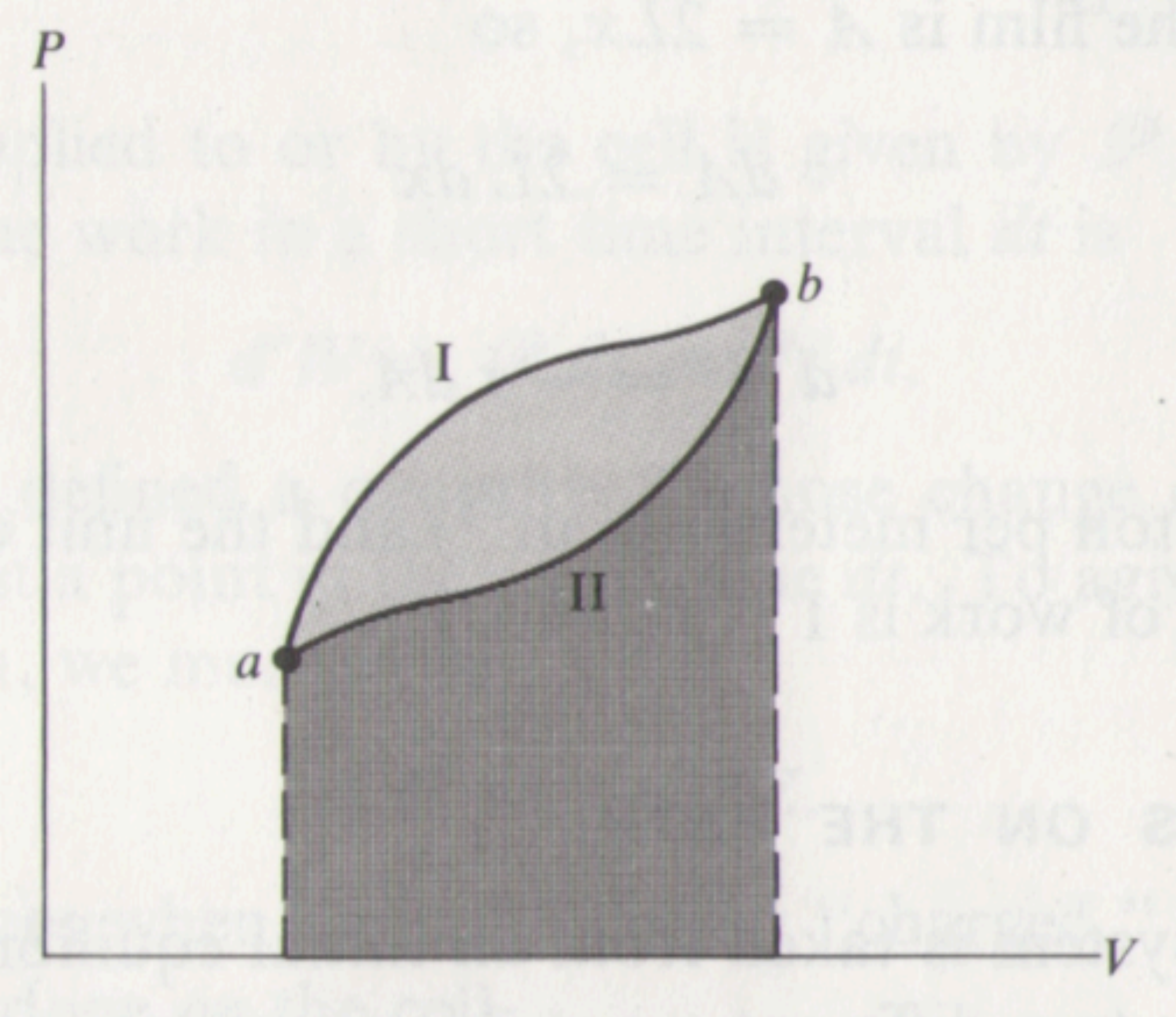


Fig. 3–7 Work depends upon the path.

$$W = \int_{V_a}^{V_b} dW = \int_{V_a}^{V_b} P dV$$

(I+II) path = cyclic process

$$W_{\text{cyclic}} = \oint \delta W = \oint P dV$$

$$a \xrightarrow{I} b \xrightarrow{II} a$$

work is done by the system

$$a \xrightarrow{II} b \xrightarrow{I} a$$

work is done on the system

Configuration work and dissipative work

Configuration work:

$$\delta W = Y_1 dX_1 + Y_2 dX_2 + ... = \sum Y_i dX_i$$

$$\begin{aligned} X_i &= \text{extensive variables } (V, M, A) \\ Y_i &= \text{intensive variables } (P, H, \sigma) \end{aligned}$$

Each product is taken with proper algebraic sign

The extensive properties $X_1, X_2, ...$ are said to determine the configuration of the system and the work $\sum Y_i dX_i$ is called the configuration work

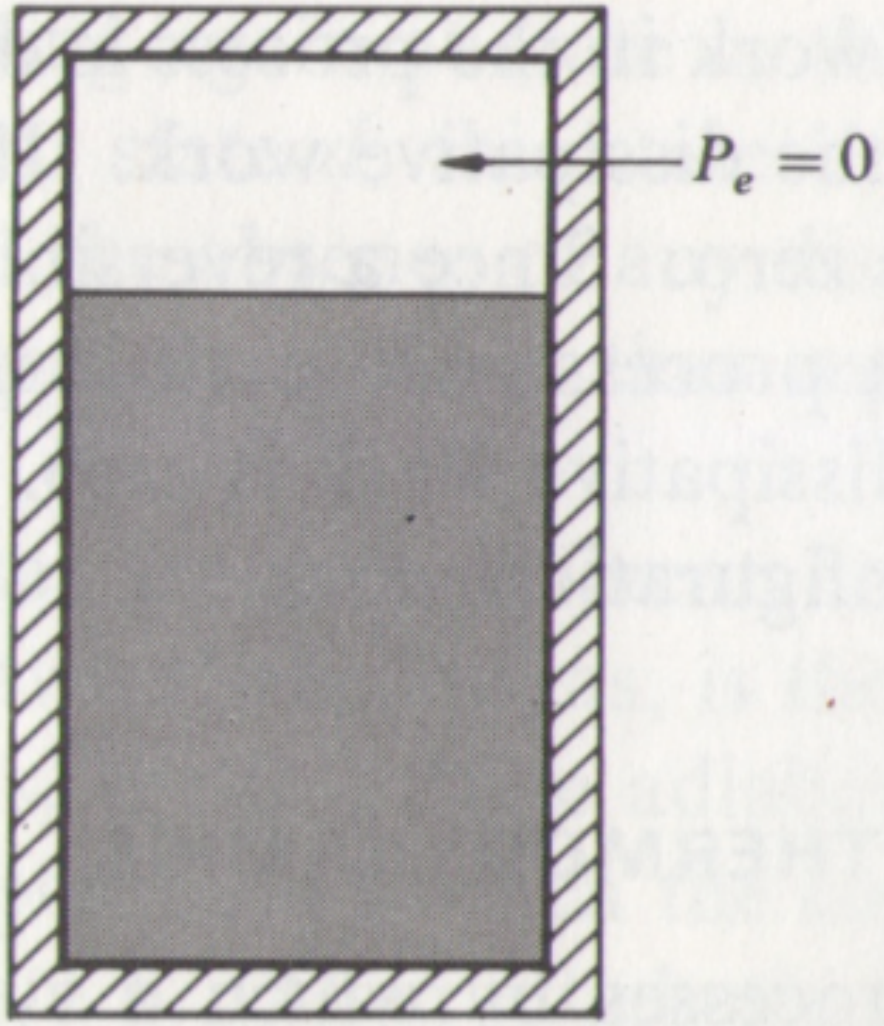


Fig. 3–8 In a free expansion of a gas, the configuration work is zero since P_e is zero.

It is possible that the configuration of the system can change without performance of the work

$$W = \int P_{\text{ext}} dV = 0$$

Dissipative work

An example of dissipative work: stirring a a cup of coffee. The work is done on the system of fluid and stirrer

One more example: the work needed to maintain a current I in a resistor R. The work is done on the resistor.

Unlike configuration work, the dissipative work cannot be expressed in terms of change of some property of the system on which the work is done.

Any process in which dissipative work is done is necessarily irreversible

The first law of thermodynamics

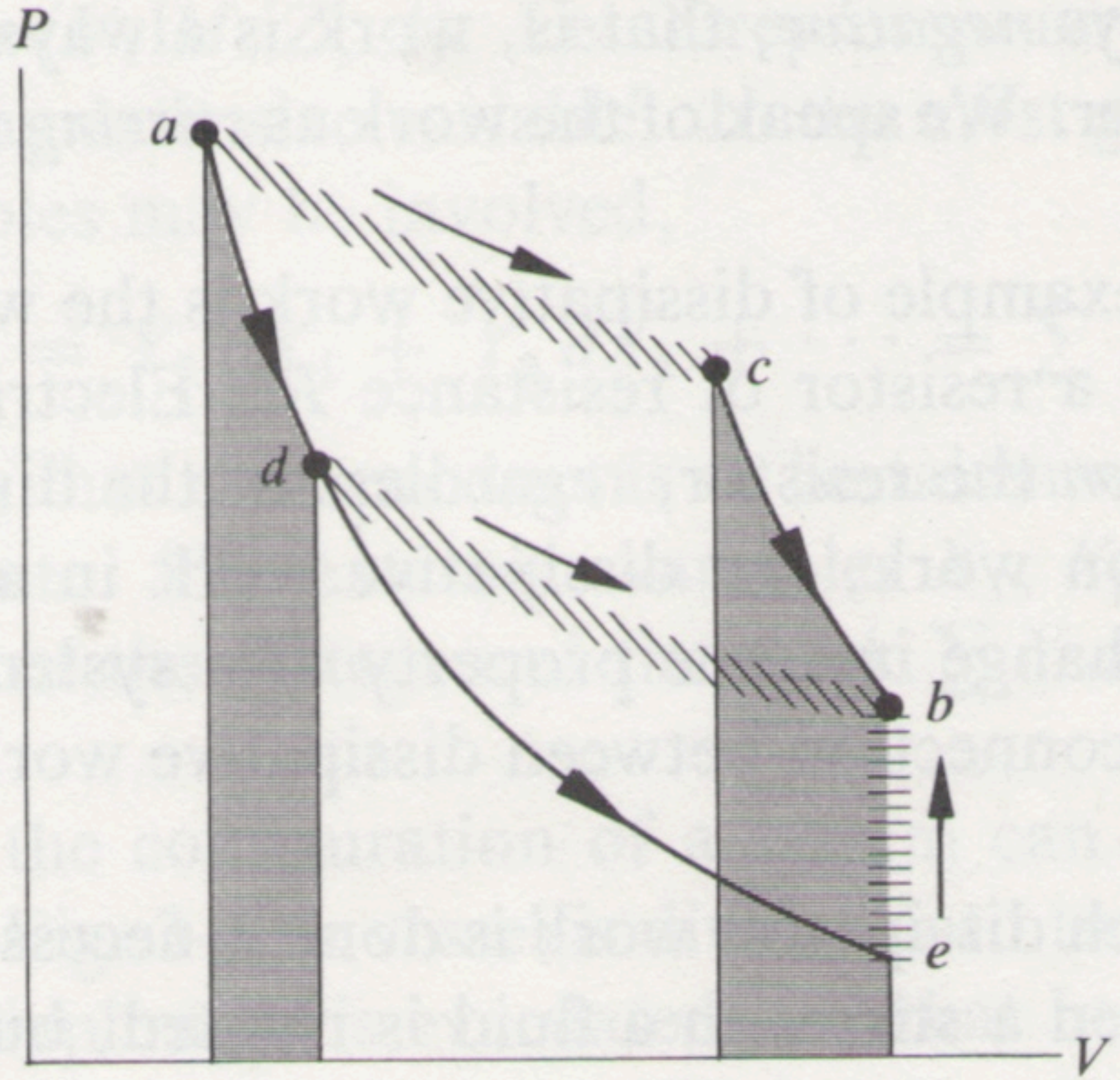


Fig. 3–9 The same amount of work is done in all adiabatic processes between the same pair of equilibrium states.

First process:
a->c: adiabatic free expansion,
c->b: reversible adiabatic expansion

Second process:
a->d: reversible adiabatic expansion,
d->b: adiabatic free expansion

Third process:
a->e: reversible adiabatic expansion,
e->b: dissipative work on the system

Experimentally:
the work done by the system in d->e is equal to the work done on the system in e->b

1st law: he total work is the same in all adiabatic processes between two equilibrium states having the same kinetic and potential energy

Internal energy

In general, the differential δW is not exact but the differential dW_{ad} is exact in the sense that that the work is the same along all adiabatic paths between given pair of states with the same kinetic and potential energies

$$W_{\text{ad}} = \int_a^b \delta W_{\text{ad}} = \int_a^b dW_{\text{ad}}$$

Internal energy U: property of the system such that the difference between its values at ***a*** and ***b*** is equal to the work done by the system along any adiabatic path from ***a*** to ***b***

$$dU = -dW_{\text{ad}} \;\Rightarrow\; \int_a^b dU = U_b - U_a = -\int_a^b dW_{\text{ad}} = -W_{\text{ad}} \;\Rightarrow\; U_a - U_b = W_{ad}$$

Statistical thermodynamics: internal energy of the system is a sum of energies of the particles from which the system is composed.

Heat flow

W = work in a non-adiabatic process between a give pair of equilibrium states

W_{ad} = work in an adiabatic process between this pair of states

Heat flow: $Q \equiv W - W_{\mathrm{ad}}$

Q>0: heat flows into the system, Q<0: heat flows out of the system

$$W_{\mathrm{ad}}(a \to b) = U_b - U_a = Q - W$$

The increase in internal energy of the system, in any process in which there is no change in the kinetic and potential energies of the system, equals to the net heat flow into the system minus the total work done by the system

Differential form of 1st law: $dU = \delta Q - \delta W$

For a reversible process, the only work is a configuration work

$$dU = \delta Q - \sum Y_i dX_i$$

Example: for a P-V-T system $dU = \delta Q - PdV$

Heat flow depends on the path

1st law: $\delta Q = dU + \delta W$

The net heat flow into a system in any process between states a and b is

$$\delta Q = dU + \delta W \quad \Rightarrow \quad Q = \int_a^b (dU + \delta W) \; = \; U_b - U_a + \int_a^b \delta W \; = \; U_b - U_a + W$$

Heat, like work, is a path function, not a point function

For a cyclic process $U_b = U_a$ so $Q = W$ and

the heat flow into the system is equal to the work done by the system

The mechanical equivalent of heat

Compare

a->b: dissipative work in the adiabatic process on system in constant configuration $U_b - U_a \;=\; |W_d|$

a->b: dissipative work = configuration work =0, but there is heat flow

$$U_b - U_a \;=\; Q$$

"Work is converted to heat": change in U due to work is the same as change due to heat flow

Unit: 1 calorie = amount of heat to warm 1 gram of water by 1C

SI unit: 1 calorie = 4.19 J

Heat capacity

Mean heat capacity $\bar{C} = \frac{Q}{\Delta T}$

``True" heat capacity $C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T} = \frac{\delta Q}{dT}$

Heat capacity depends on the process

Heat capacity at constant pressure: $C_P = \left(\frac{\delta Q}{dT}\right)_P$

Heat capacity at constant volume: $C_V = \left(\frac{\delta Q}{dT}\right)_V$

Later: if we know C_P and the equation of state,
we can find the heat capacity for any other process

Specific heat capacity: heat capacity per unit mass or per kmole

$$\mathrm{SI}: \quad 1\frac{J}{Kkg} \quad \text{or} \quad 1\frac{J}{Kkmol}$$

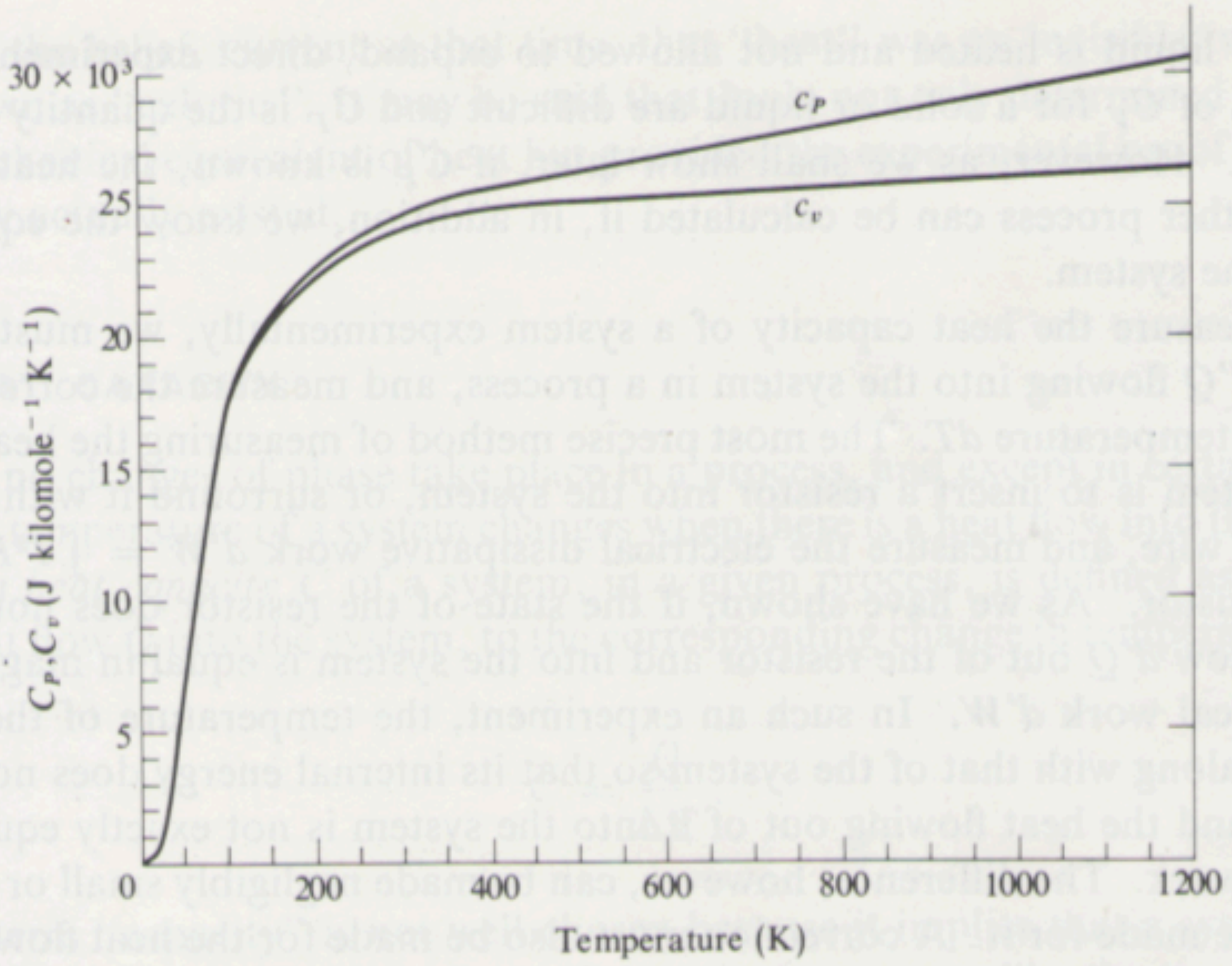


Fig. 3–10 Graphs of c_v and c_P for copper as functions of temperature at a constant pressure of 1 atm.

Dulong-Petit value $\simeq 3R$

Later: on theoretical grounds $c_v \simeq 3R$ is expected at high T

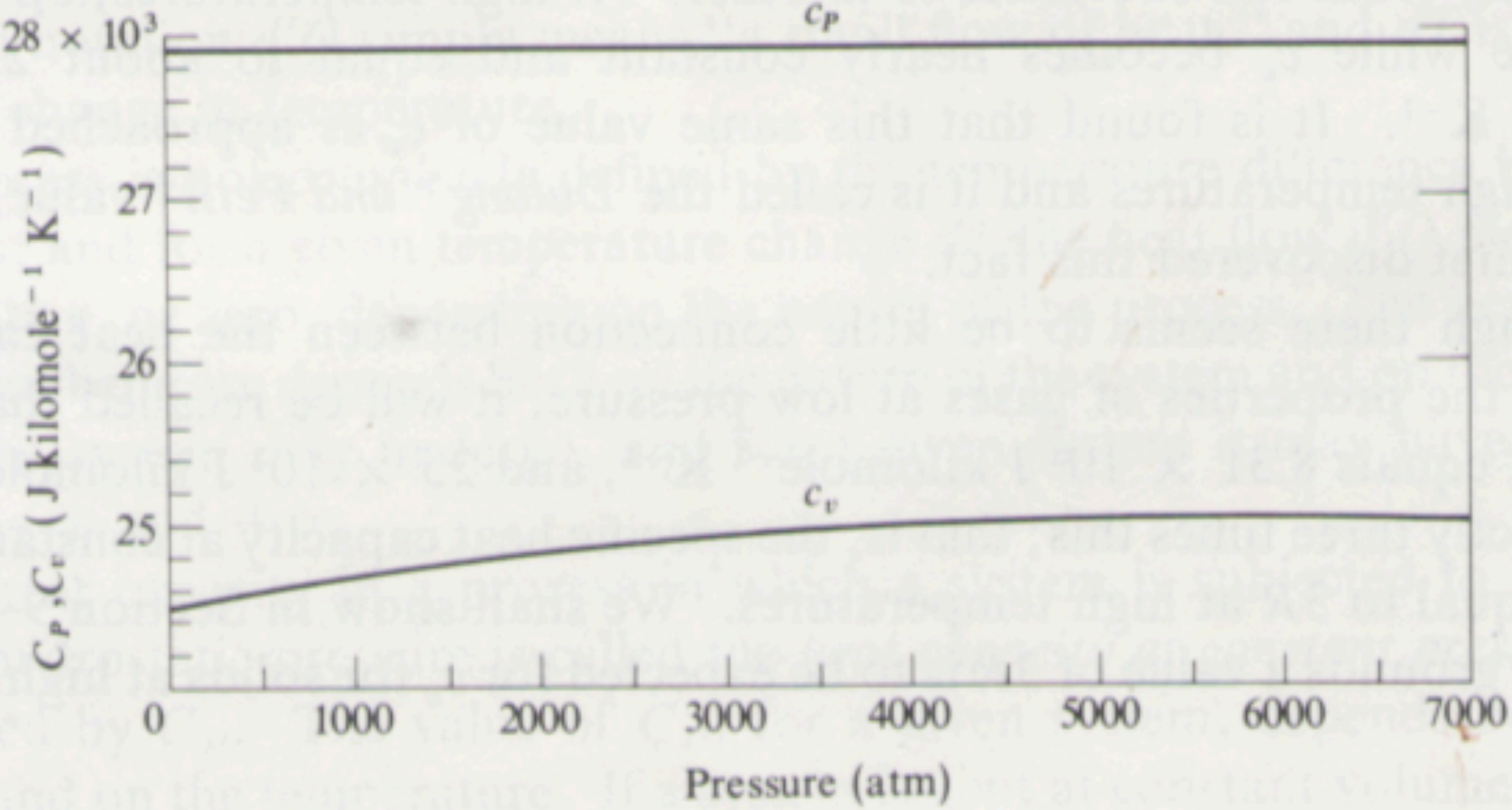


Fig. 3–11 Graphs of c_v and c_P for mercury as functions of pressure at a constant temperature of 0°C.

Heat reservoir: a system with very large heat capacity (no change of temperature due to heat flow in or out).

Heat of transformation and enthalpy

Heat of transformation = ratio of the heat absorbed to mass undergoing the phase transition $l = \frac{\delta Q}{m}$

$$\text{Units}: \quad 1\frac{J}{kg} \quad \text{or} \quad \frac{1J}{kmol}$$

Change of phase is always associated with change of volume

$$\Rightarrow \quad W = P(V_2 - V_1) \quad \Leftrightarrow \quad w = P(v_2 - v_1)$$

From the 1st law $\quad u_2 - u_1 = l - P(v_2 - v_1)$

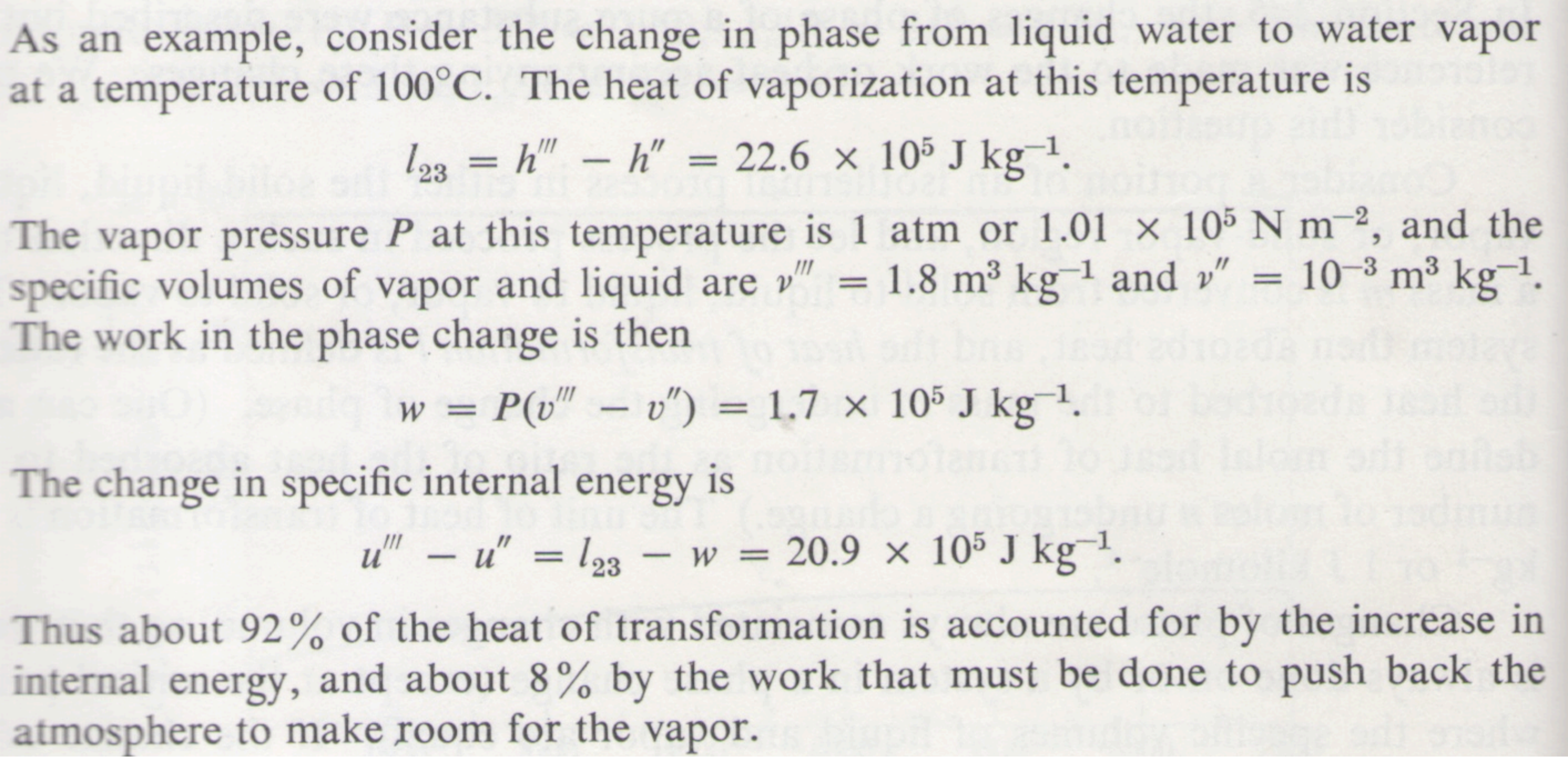
$$\Leftrightarrow \quad l = h_2 - h_1, \quad h \equiv u + Pv \quad \text{“enthalpy''}$$

Enthalpy is a function of state. Later: the heat flow in any reversible isobaric process is equal to change in enthalpy.

$$l_{12} \equiv \text{heat of fusion} \quad (\text{solid} \rightarrow \text{liquid})$$

$$l_{23} \equiv \text{heat of vaporization} \quad (\text{liquid} \rightarrow \text{vapor})$$

$$l_{13} \equiv \text{heat of sublimation} \quad (\text{solid} \rightarrow \text{vapor})$$



As an example, consider the change in phase from liquid water to water vapor at a temperature of 100°C. The heat of vaporization at this temperature is

$$l_{23} = h''' - h'' = 22.6 \times 10^5\ \mathrm{J\ kg^{-1}}.$$

The vapor pressure P at this temperature is 1 atm or $1.01 \times 10^5\ \mathrm{N\ m^{-2}}$, and the specific volumes of vapor and liquid are $v''' = 1.8\ \mathrm{m^3\ kg^{-1}}$ and $v'' = 10^{-3}\ \mathrm{m^3\ kg^{-1}}$. The work in the phase change is then

$$w = P(v''' - v'') = 1.7 \times 10^5\ \mathrm{J\ kg^{-1}}.$$

The change in specific internal energy is

$$u''' - u'' = l_{23} - w = 20.9 \times 10^5\ \mathrm{J\ kg^{-1}}.$$

Thus about 92% of the heat of transformation is accounted for by the increase in internal energy, and about 8% by the work that must be done to push back the atmosphere to make room for the vapor.

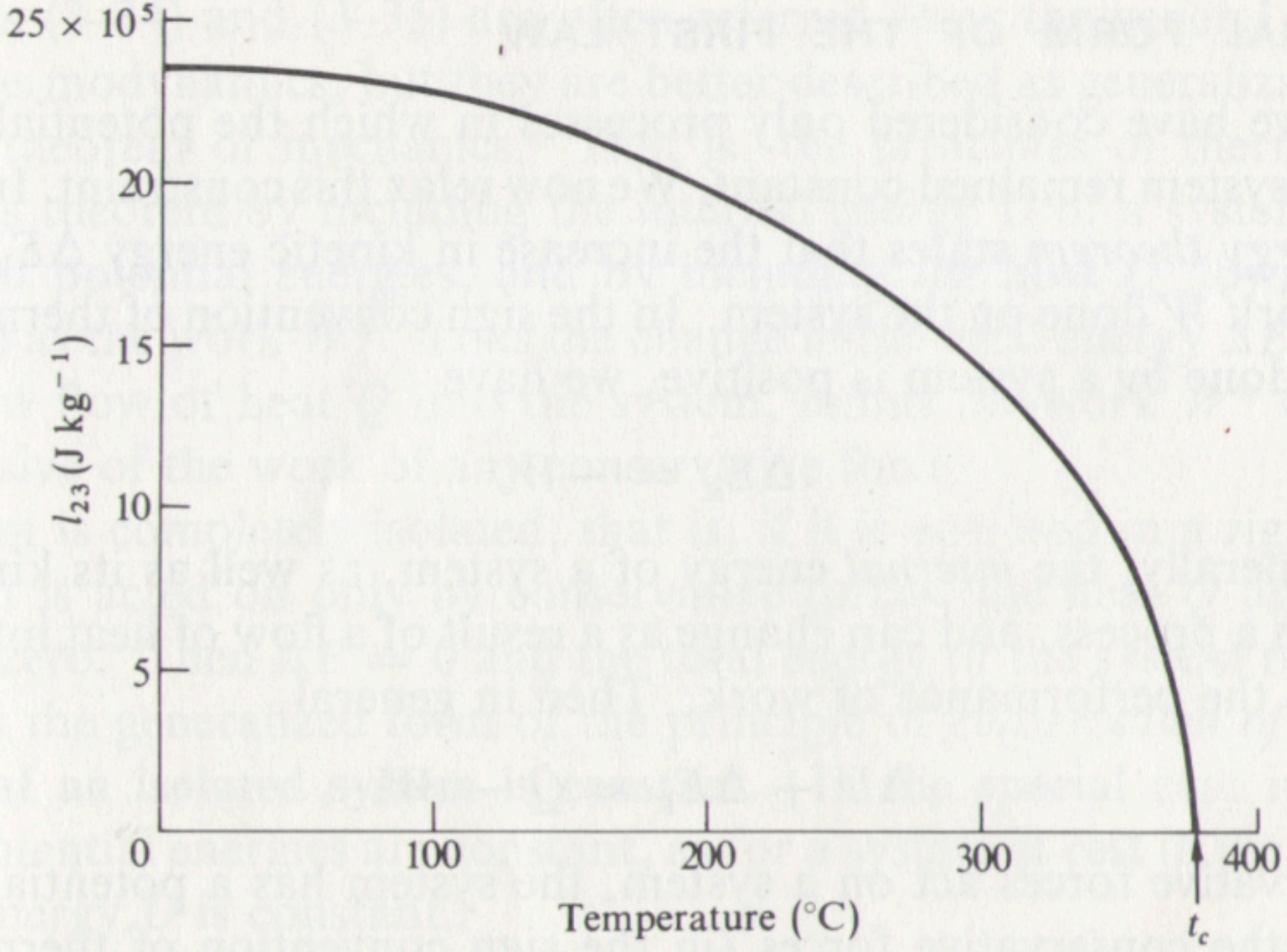


Fig. 3–12 Latent heat of vaporization of water as a function of temperature. The latent heat becomes zero at the critical temperature $t_c = 374$°C.

Consider a cyclic process around the triple point so the only changes in enthalpy occur during phase transitions

1. Solid -> vapor: heat flow into the system $\Delta h_1 \;=\; l_{13}$

2. Vapor -> liquid: heat flow out of the system $\Delta h_2 \;=\; -\,l_{23}$

3. Liquid -> solid: heat flow out of the system $\Delta h_3 \;=\; -\,l_{12}$

Enthalpy is a function of state $\Rightarrow$ does not change in a cyclic process

$$\Rightarrow \quad l_{13} \;=\; l_{12} + l_{23}$$

General form of the first law

If there is a change of the kinetic energy of the system

$$\Delta U + \Delta E_k \; = \; Q - W$$

If conservative forces act on the system, the system has a potential energy and the work of conservative forces equals to (+) change of the potential energy

$$\text{If} \;\; W^* \; \equiv \; W - W_c,$$

$$\text{then} \quad \Delta U + \Delta E_k \; = \; Q - W^* - W_c \quad \Leftrightarrow \quad \Delta U + \Delta E_k + \Delta E_p \; = \; Q - W^*$$

$$\text{Total energy of the system} \quad E \; \equiv \; U + E_k + E_p$$

If E_b and E_a represent the final and initial values of total energy a process

$$\Delta E \; = \; E_b - E_a \; = \; Q - W^*$$

- general form of the 1st law of thermodynamics

For infinitesimal changes $dE \; = \; \delta Q - \delta W^*$

Example: energy equation of steady flow

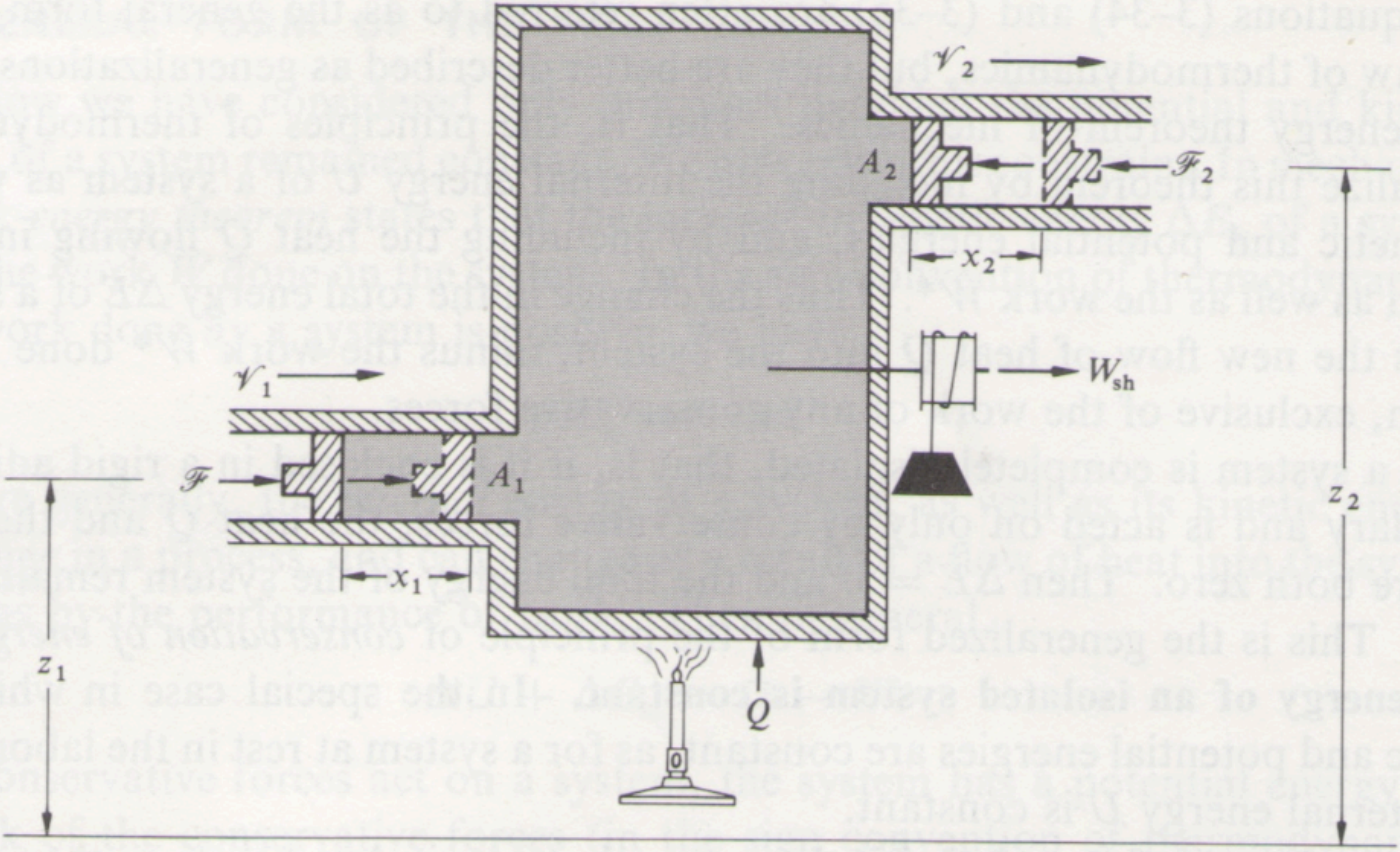


Fig. 3–13 Steady flow process.

$$W = W_{\mathrm{sh}} + P_2V_2 - P_1V_1 + mg(z_2 - z_1)$$

Total work - (work of conservative forces) = $W^* \ = \ W_{\text{sh}} + P_2V_2 - P_1V_1$

$$
\begin{aligned}
\Delta E \ &= \ m(u_2 - u_1) && : && \text{increase in internal energy of mass } m \\
\Delta E_k \ &= \ \frac{m}{2}(\mathcal{V}_2^2 - \mathcal{V}_1^2) && : && \text{increase in kinetic energy of mass } m \\
\Delta E_\nu \ = \ mg(z_2 - z_1) \ &= \ W_c && : && \text{increase in poyential energy of mass } m
\end{aligned}
$$

$$\Delta E \ = Q - W^* \ \Rightarrow$$

$$m(u_2 - u_1) + \frac{m}{2}(\mathcal{V}_2^2 - \mathcal{V}_1^2) + mg(z_2 - z_1) \ = \ Q - W_{\text{sh}} - P_2V_2 + P_1V_1$$

$\text{Per unit mass :} \quad V_2 = mv_2, \quad V_1 = mv_1, \quad Q = mq, \quad W_{\text{sh}} = mw_{\text{sh}}$

$$\left(u_2 + Pv_2 + \frac{1}{2}\mathcal{V}_2^2 + gz_2\right) - \left(u_1 + Pv_1 + \frac{1}{2}\mathcal{V}_1 + gz_1\right) = q - w_{\text{sh}}$$

$u + Pv \equiv h \quad : \quad$ specific enthalpy

⇒ Energy equation for steady flow:

$$\left(h_2 + \frac{1}{2}\mathcal{V}_2^2 + gz_2\right) - \left(h_1 + \frac{1}{2}\mathcal{V}_1 + gz_1\right) = q - w_{\text{sh}}$$

Examples

1. **The turbine:**

$$q \simeq 0, \quad z_2 \simeq z_1 \quad \Rightarrow \quad -w_{\rm sh} \;=\; (h_2 - h_1) + \frac{1}{2}(\mathcal{V}_2^2 - \mathcal{V}_1^2)$$

2. **Flow through a nozzle:**

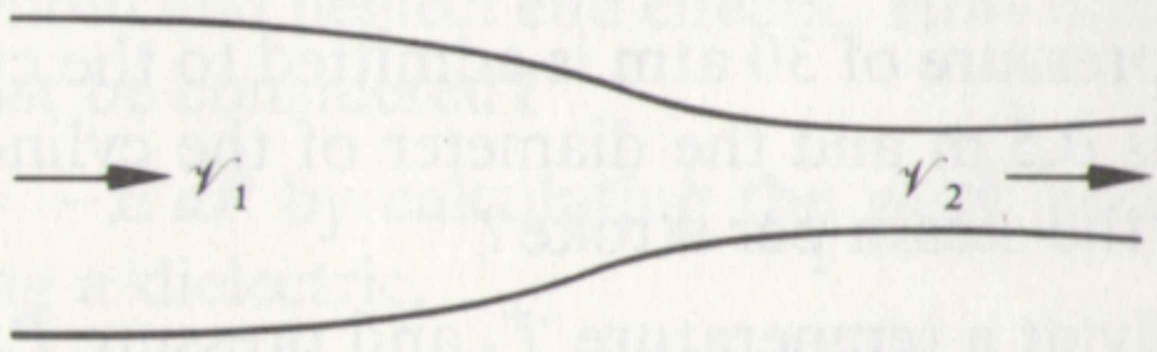


Fig. 3–14 Flow through a nozzle.

$$w_{\rm sh} \;\simeq 0, \quad q \simeq 0 \quad \Rightarrow$$

$$\mathcal{V}_2^2 = \mathcal{V}_1^2 + 2(h_2 - h_1)$$

3. **Bernoulli's equation for pipe of variable cross section and elevation:**

$$w_{\rm sh} \;\simeq 0, \quad q \simeq 0 \quad \Rightarrow \quad h_2 + \frac{1}{2}\mathcal{V}_2^2 + g z_2 \;=\; h_1 + \frac{1}{2}\mathcal{V}_1^2 + g z_1$$

$$\Rightarrow \; u + Pv + \frac{1}{2}\mathcal{V}^2 + gz \;=\; \text{const}$$

If change of u = heat flow - config. work - dissipative work = 0, then

$$Pv + \frac{1}{2}\mathcal{V}^2 + gz \;=\; \text{const} \quad \Leftrightarrow \quad P + \frac{\rho}{2}\mathcal{V}^2 + \rho g z = \; \text{const}$$

Energy equation u = u(P,v,T)

Since equation of state is f(P,v,T)=0,
we can consider u(T,v) or u(T,P), or u(P,v)

1. u = u(T,v)

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$\text{From the 2nd law : equation of state} \Rightarrow \left(\frac{\partial u}{\partial v}\right)_T$$

$$\left(\frac{\partial u}{\partial v}\right)_T = ? \qquad \text{1st law} \Rightarrow \delta q = du + Pdv$$

$$\Rightarrow \delta q = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv$$

$$\text{Constant volume : } dv = 0, \ \delta q = c_v dT$$

$$\Rightarrow c_v dT_v = \left(\frac{\partial u}{\partial T}\right)_v dT_v \Rightarrow c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

$\Rightarrow$ For any reversible process $\delta q = c_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv$

At constant pressure : $\delta q = c_P dT$

$$\Rightarrow \quad c_P dT_P = c_v dT_P + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv_P$$

$$\Rightarrow \quad c_P - c_v = \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] \left(\frac{dv}{dT}\right)_P$$

At constant temperature : $dT = 0 \Rightarrow$

$$\delta q_T = \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv_T = \left(\frac{\partial u}{\partial v}\right)_T dv_T + P dv_T$$

For a reversible adiabatic process : $\delta q = 0$

$$\Rightarrow \quad c_v \left(\frac{\partial T}{\partial v}\right)_s = -\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]$$

2. u = u(T,P)

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

$$\text{Equation of state}: \quad \Rightarrow \quad \left(\frac{\partial h}{\partial P}\right)_T$$

$$\left(\frac{\partial h}{\partial T}\right)_P = ? \qquad h = u + Pv \quad \Rightarrow \quad dh = du + Pdv + vdP$$

$$\delta q = du + Pdv \Leftrightarrow \delta q = dh - vdP \Rightarrow \delta q = \left(\frac{\partial h}{\partial T}\right)_P dT + \left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] dP$$

$$\text{Constant pressure}: \quad dP = 0, \quad \delta q = c_P dT \quad \Rightarrow \quad \left(\frac{\partial h}{\partial T}\right)_P = c_P$$

$$\Rightarrow \ \text{For any reversible process} \quad \delta q = c_P dT + \left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] dP$$

$$\text{Constant volume}: \quad \delta q = c_v dT \quad \Rightarrow \quad c_P - c_v = -\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right]\left(\frac{\partial P}{\partial T}\right)_v$$

$$\text{Constant temperature}: \quad \delta q = \left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] dP_T$$

$$\text{Adiabatic process}: \quad \delta q = 0 \quad \Rightarrow \quad c_P\left(\frac{\partial T}{\partial P}\right)_s = -\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right]$$

3. u = u(P,v)

$$du = \left(\frac{\partial u}{\partial P}\right)_v dP + \left(\frac{\partial u}{\partial v}\right)_P dv$$

No new properties:

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$dT = \left(\frac{\partial T}{\partial P}\right)_v dP + \left(\frac{\partial T}{\partial v}\right)_P dv$$

$$\Rightarrow \quad du = \left[\left(\frac{\partial u}{\partial T}\right)_v \left(\frac{\partial T}{\partial P}\right)_v\right] dP + \left[\left(\frac{\partial u}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_P + \left(\frac{\partial u}{\partial v}\right)_T\right] dv$$

$$\Rightarrow \begin{cases} \left(\frac{\partial u}{\partial P}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v \left(\frac{\partial T}{\partial P}\right)_v \\ \left(\frac{\partial u}{\partial v}\right)_P = \left(\frac{\partial u}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_P + \left(\frac{\partial u}{\partial v}\right)_T \end{cases}$$

Mathematical digression

$$\text{Consider} \quad w = w(x,y,z) \quad \text{where} \quad f(x,y,z) = 0$$

Formula:

$$\left(\frac{\partial w}{\partial x}\right)_y = \frac{\partial w(x,y,z)}{\partial x} + \frac{\partial w(x,y,z)}{\partial z}\frac{\partial z(x,y)}{\partial x}$$

Proof: let z=z(x,y), then

$$w\big(x+dx, y, z(x+dx,y)\big) - w(x,y,z)$$

$$= \left.\frac{\partial w(x,y,z)}{\partial x}\right|_{z=z(x,y)} dx + \left.\frac{\partial w(x,y,z)}{\partial z}\right|_{z=z(x,y)} dz$$

$$= \left.\frac{\partial w(x,y,z)}{\partial x}\right|_{z=z(x,y)} dx + \left.\frac{\partial w(x,y,z)}{\partial z}\right|_{z=z(x,y)} \frac{\partial z(x,y)}{\partial x} dx$$

$$\Rightarrow \quad \left(\frac{\partial w}{\partial x}\right)_y = \frac{\partial w(x,y,z)}{\partial x} + \frac{\partial w(x,y,z)}{\partial z}\frac{\partial z(x,y)}{\partial x}$$

If $w = w(x,y,z)$ and $f(x,y,z) = 0$

$$\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial w}{\partial z}\right)_y$$

Proof:

$$\left.\begin{aligned} \left(\frac{\partial w}{\partial x}\right)_y &= \frac{\partial w(x,y,z)}{\partial x} + \frac{\partial w(x,y,z)}{\partial z}\frac{\partial z(x,y)}{\partial x} \\ \left(\frac{\partial w}{\partial z}\right)_y &= \frac{\partial w(x,y,z)}{\partial y} + \frac{\partial w(x,y,z)}{\partial x}\frac{\partial x(y,z)}{\partial z} \end{aligned}\right\} \Rightarrow$$

$$\begin{aligned} \left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y &= \left[\frac{\partial w(x,y,z)}{\partial x} + \frac{\partial w(x,y,z)}{\partial z}\frac{\partial z(x,y)}{\partial x}\right]\frac{\partial x(y,z)}{\partial z} \\ &= \frac{\partial w(x,y,z)}{\partial x}\frac{\partial x(y,z)}{\partial z} + \frac{\partial w(x,y,z)}{\partial z}\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y \\ &= \frac{\partial w(x,y,z)}{\partial z} + \frac{\partial w(x,y,z)}{\partial x}\frac{\partial x(y,z)}{\partial z} = \left(\frac{\partial w}{\partial z}\right)_y \end{aligned}$$

Using these formulas, one can prove

$$\left(\frac{\partial u}{\partial P}\right)_v = c_v\left(\frac{\partial T}{\partial P}\right)_v,$$

$$\left(\frac{\partial h}{\partial v}\right)_P = c_P\left(\frac{\partial T}{\partial v}\right)_P,$$

$$c_v\left(\frac{\partial P}{\partial v}\right)_s = c_P\left(\frac{\partial P}{\partial v}\right)_T,$$

$$\delta q_T = c_P\left(\frac{\partial T}{\partial v}\right)_P dv_T + c_v\left(\frac{\partial T}{\partial P}\right)_v dP_T$$

Proof of $c_v\left(\dfrac{dP}{dv}\right)_s = c_P\left(\dfrac{dP}{dv}\right)_T$

Take T and v independent: P = P(T,v) and u = u(T,v)

In the adiabatic process

$$0 = dQ = du + Pdv = u(v+dv, T+dT) - u(P,v) + Pdv$$

$$= \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]dv \;\Rightarrow\; dT_s = -\frac{1}{c_v}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]dv_s$$

Using this formula we get

$$dP_s = P(v+dv, T+dT) - P(v,T) = \left(\frac{\partial P}{\partial v}\right)_T dv_s + \left(\frac{\partial P}{\partial T}\right)_v dT_s$$

$$\Rightarrow \left(\frac{\partial P}{\partial v}\right)_s \equiv \frac{dP_s}{dv_s} = \left(\frac{\partial P}{\partial v}\right)_T - \frac{1}{c_v}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]$$

$$\Rightarrow \text{l.h.s} = c_v\left(\frac{\partial P}{\partial v}\right)_s = c_v\left(\frac{\partial P}{\partial v}\right)_T - \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]\left(\frac{\partial P}{\partial T}\right)_v$$

Consider now r.h.s.

$$\text{r.h.s.} \;=\; c_P\left(\frac{\partial P}{\partial v}\right)_T \;=\; \left\{c_v + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]\left(\frac{\partial v}{\partial T}\right)_P\right\}\left(\frac{\partial P}{\partial v}\right)_T$$

From cyclic formula on p. 34 and inversion formula on p.35

$$\left(\frac{\partial v}{\partial T}\right)_P \;=\; \frac{-1}{\left(\frac{\partial P}{\partial v}\right)_T\left(\frac{\partial T}{\partial P}\right)_v} = -\frac{\left(\frac{\partial P}{\partial T}\right)_v}{\left(\frac{\partial P}{\partial v}\right)_T}$$

$$\Rightarrow \quad \text{r.h.s.} \;=\; \left(\frac{\partial P}{\partial v}\right)_T\left\{c_v - \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]\frac{\left(\frac{\partial P}{\partial T}\right)_v}{\left(\frac{\partial P}{\partial v}\right)_T}\right\}$$

$$= \; c_v\left(\frac{\partial P}{\partial v}\right)_T - \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]\left(\frac{\partial P}{\partial T}\right)_v \;=\; \text{l.h.s.}$$

$$\text{Later : eqn. of state + 2nd law} \Rightarrow \left(\frac{du}{dv}\right)_T \text{ and } \left(\frac{dh}{dP}\right)_T$$

$$\text{How to measure } \left(\frac{du}{dv}\right)_T \text{ and } \left(\frac{dh}{dP}\right)_T \text{ experimentally?}$$

Energy equation $u = u(P, v, T) \;\Rightarrow\; P = p(u, v, T)$
Equation of state $f(P, v, T) = 0 \;\Rightarrow\; f(p(u, v, T), v, T) = F(u, v, T) = 0$

$$\Rightarrow \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_u \left(\frac{\partial T}{\partial u}\right)_v = -1 \Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = -c_v \left(\frac{\partial T}{\partial v}\right)_u$$

Similarly $h = h(P, v, T) \;\Rightarrow\; G(h, v, T) = 0$

$$\Rightarrow \left(\frac{\partial h}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_h \left(\frac{\partial T}{\partial h}\right)_P = -1 \Rightarrow \left(\frac{\partial h}{\partial P}\right)_T = -c_P \left(\frac{\partial T}{\partial P}\right)_h$$

Gay-Lussac and Joule measured $\left(\frac{\partial T}{\partial v}\right)_u$

Gay-Lussac-Joule experiment

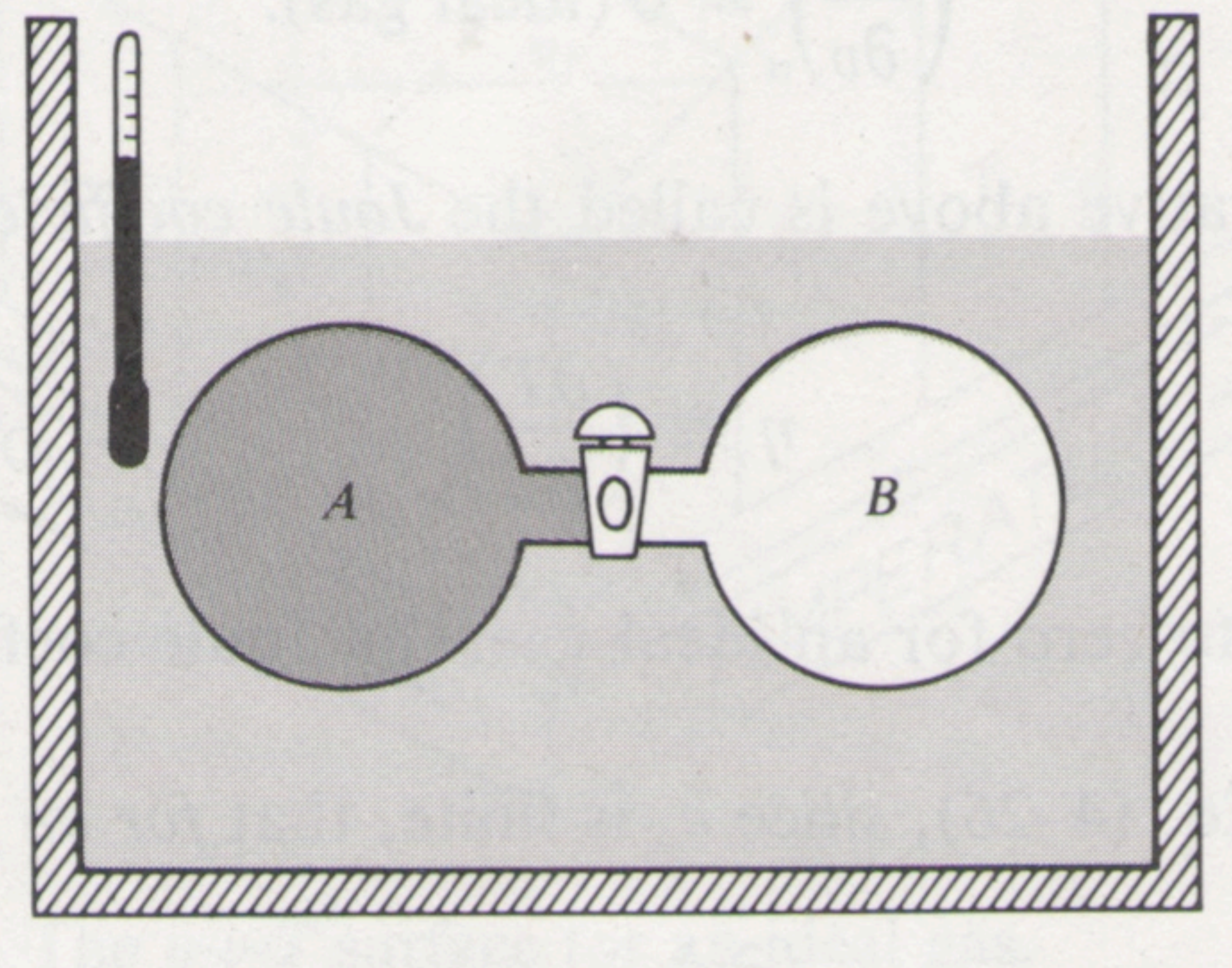


Fig. 4–1 Principle of the Gay-Lussac–Joule experiment.

Ideal gas :

$$\left(\frac{\partial T}{\partial v}\right)_u = 0$$

$$\text{In general : } \quad \eta \equiv \left(\frac{\partial T}{\partial v}\right)_u \neq 0 \qquad \text{“Joule coefficient}''$$

$$\text{For an ideal gas :} \quad \left(\frac{\partial T}{\partial v}\right)_u = 0 \quad \Rightarrow \quad \left(\frac{\partial u}{\partial v}\right)_T = 0$$

Specific internal energy of an ideal gas is independent of the volume and is a function of the temperature only

$$c_v = \frac{du}{dT} \quad \Leftrightarrow \quad du = c_v dT \quad \Rightarrow$$

$$u - u_0 = \int_{u_0}^{u} du = \int_{T_0}^{T} c_v \, dT \quad \Rightarrow \quad u = u_0 + c_v(T - T_0)$$

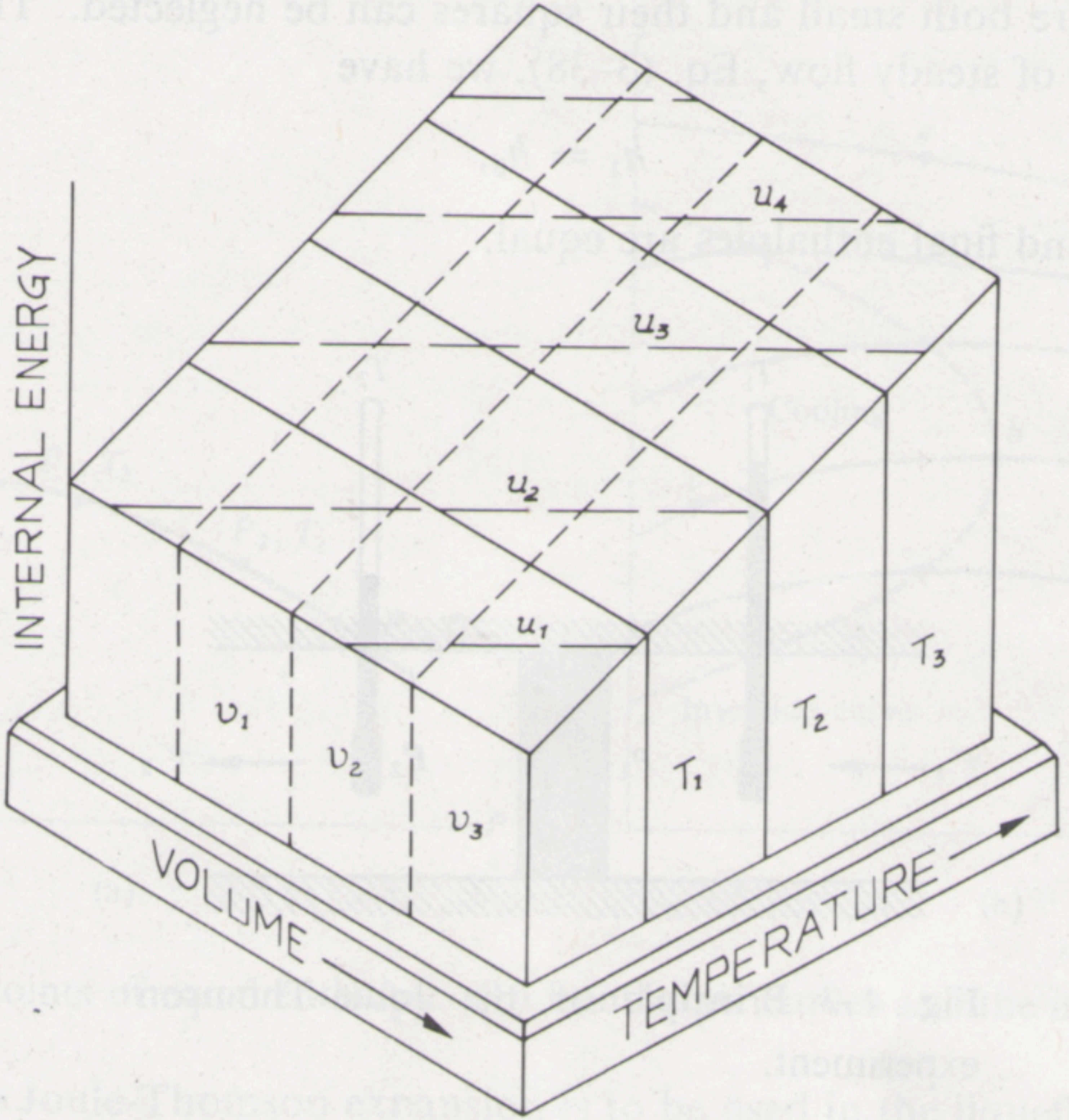


Fig. 4–2 The *u-v-T* surface for an ideal gas.

Joule-Thomson experiment

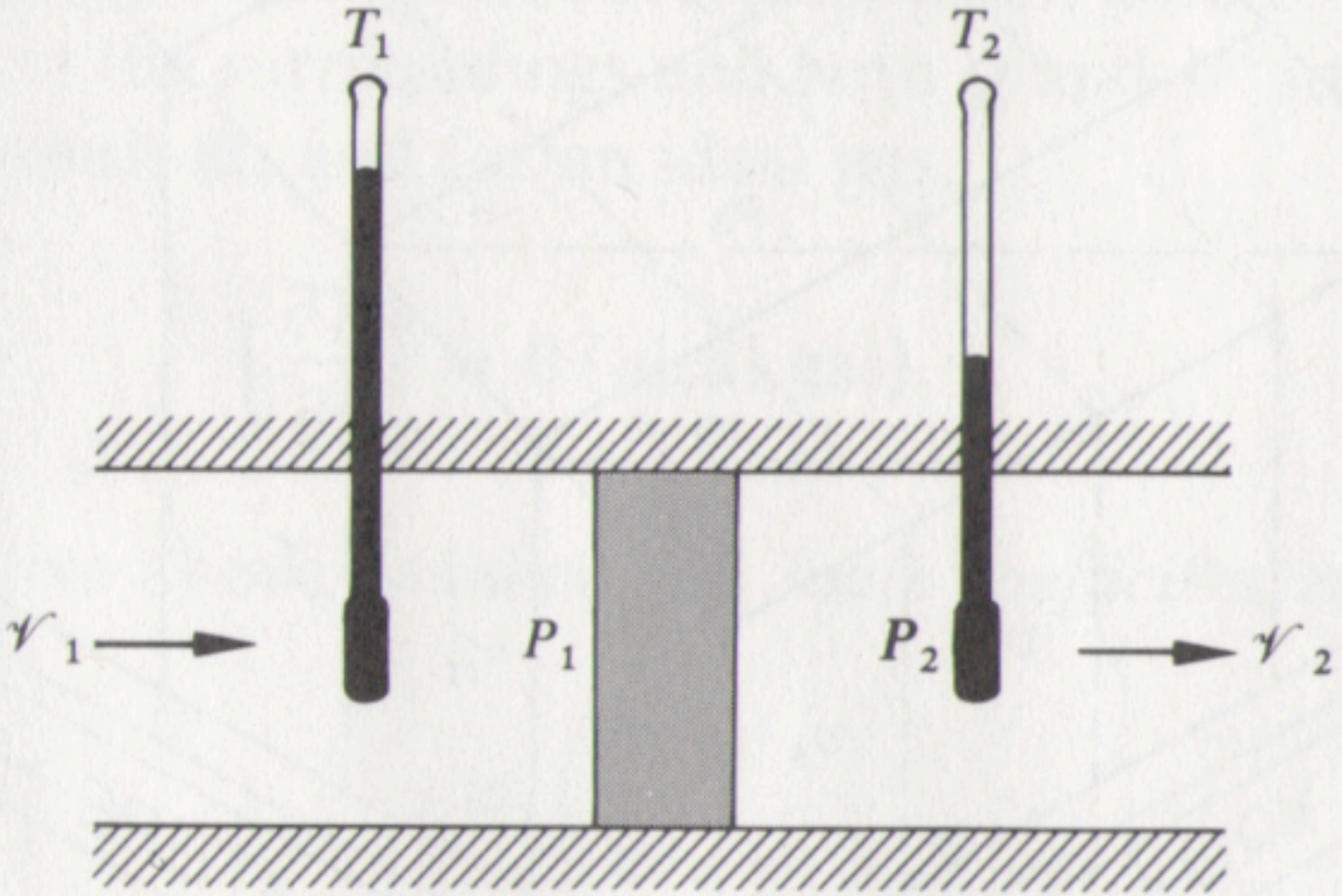


Fig. 4–3 Principle of the Joule-Thomson experiment.

Steady flow,

$$Q = W_{\rm sh} = 0,$$

No change in elevation,

Velocities are small

$$\Rightarrow \quad h_1 = h_2$$

Keep P_1, T_1 but vary pumping rate so P_2 changes

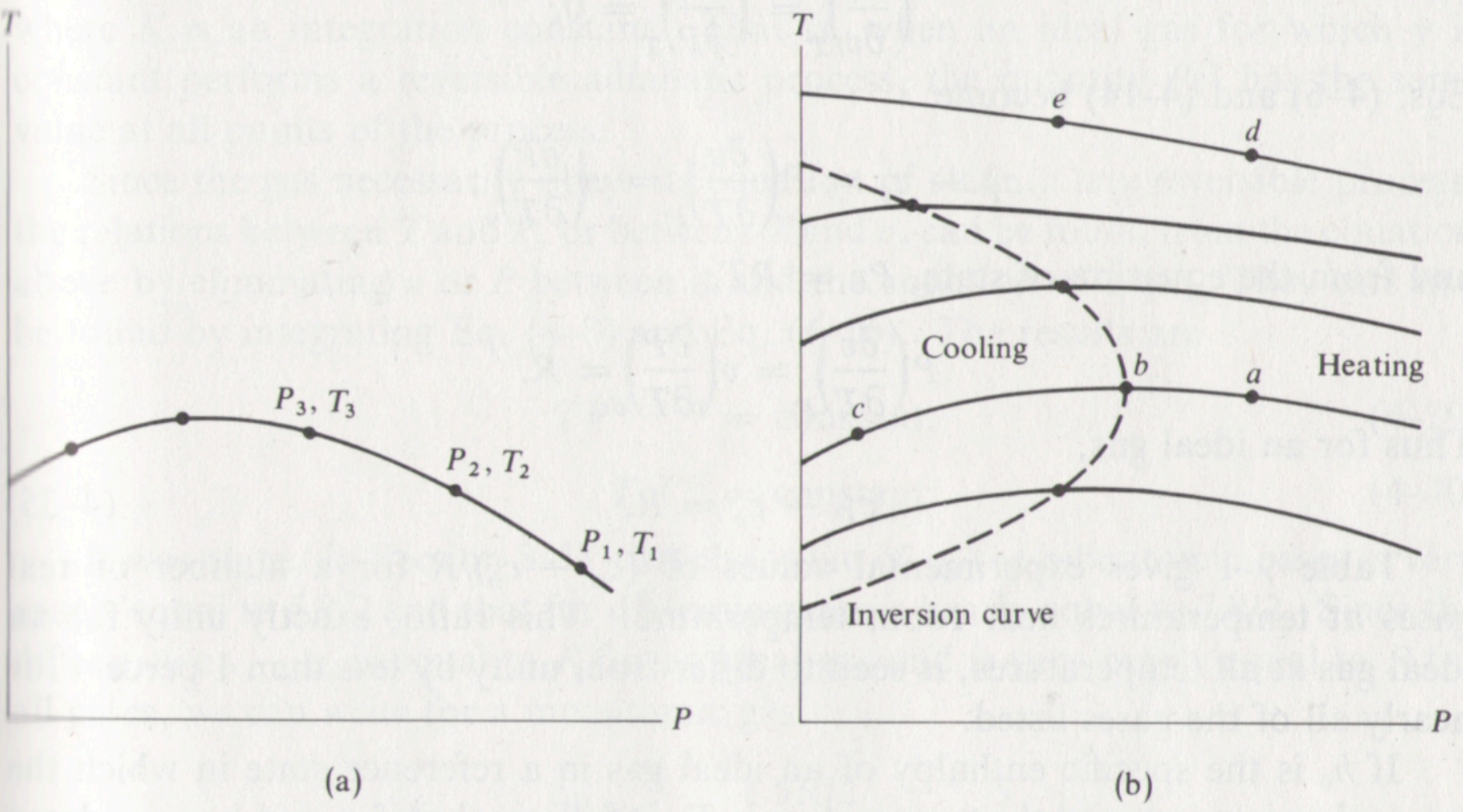


Fig. 4–4 (a) Points of equal enthalpy. (b) Isenthalpic curves and the inversion curve.

a->b or b->c: drop in temperature,
d->e: rise in temperature

$$\text{Joule} - \text{Thomson coefficient} \quad \mu \equiv \left(\frac{\partial T}{\partial P}\right)_h$$

Experimentally, for an ideal gas $\mu = 0 \quad \Rightarrow \quad \left(\frac{\partial h}{\partial P}\right)_T = 0$

Later: μ can be calculated from the equation of state

$$\text{For an ideal gas :} \quad \left(\frac{\partial h}{\partial P}\right)_T = 0$$

$$\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial h}{\partial P}\right)_T = 0 \quad \Rightarrow \quad c_P - c_v = P\left(\frac{\partial v}{\partial T}\right)_P = v\left(\frac{\partial P}{\partial T}\right)_v$$

$$Pv = RT \quad \Rightarrow \quad P\left(\frac{\partial v}{\partial T}\right)_P = v\left(\frac{\partial P}{\partial T}\right)_v \quad \Rightarrow \quad c_P - c_v = R$$

Suppose h_0 is the specific enthalpy of an ideal gas in a reference state in which the internal energy is u_0 and the temperature T_0.

If c_P is constant, the enthalpy equation of an ideal gas is

$$h = h_0 + c_P(T - T_0)$$

Reversible adiabatic processes

$$\left(\frac{\partial P}{\partial v}\right)_s = \frac{c_P}{c_v}\left(\frac{\partial P}{\partial v}\right)_T$$

For an ideal gas $\left(\frac{\partial P}{\partial v}\right)_T = -\frac{P}{v} \quad \Rightarrow \quad \frac{dP}{P} + \gamma\frac{dv}{v} = 0, \quad \gamma \equiv \frac{c_P}{c_v}$

$$\Rightarrow \ln P + \gamma \ln v = \text{const} \quad \Leftrightarrow \quad Pv^{\gamma} = \text{const}$$

For monoatomic gases $c_v = \frac{3}{2}R \quad \Rightarrow \quad \gamma = \frac{c_v + R}{c_v} = \frac{5}{3},$

for diatomic gases $c_v = \frac{5}{2}R \quad \Rightarrow \quad \gamma = \frac{c_v + R}{c_v} = \frac{7}{5}$

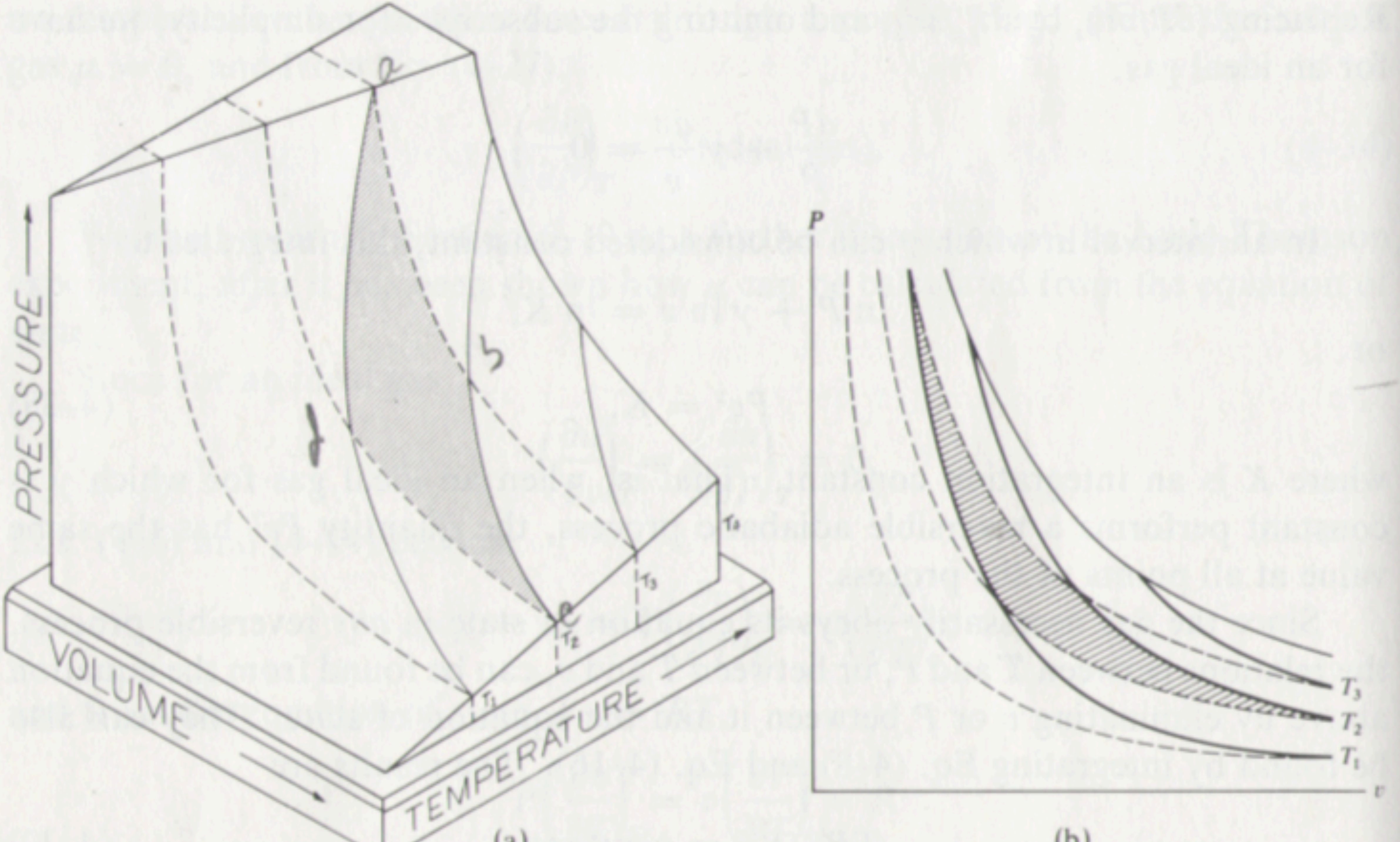
The specific work in a reversible adiabatic expansion of an ideal gas

$$Pv^{\gamma} = K \quad \Rightarrow$$

$$w = \int_{v_1}^{v_2} dv\ P = K\int_{v_1}^{v_2} dv\ v^{-\gamma} = \frac{K}{1-\gamma}\left(v_2^{1-\gamma} - v_1^{1-\gamma}\right) = \frac{P_2 v_2 - P_1 v_1}{1-\gamma}$$

Obviously, also $w = u_2 - u_1 \ - \ c_v(T_2 - T_1)$

Carnot cycle:



(a) (b)

Fig. 4–5 (a) Adiabatic processes (full lines) on the ideal gas *P-v-T* surface. (b) Projection of the adiabatic processes in (a) onto the *P-v* plane. The shaded area is a Carnot cycle (see Section 4–7).

Carnot cycle:

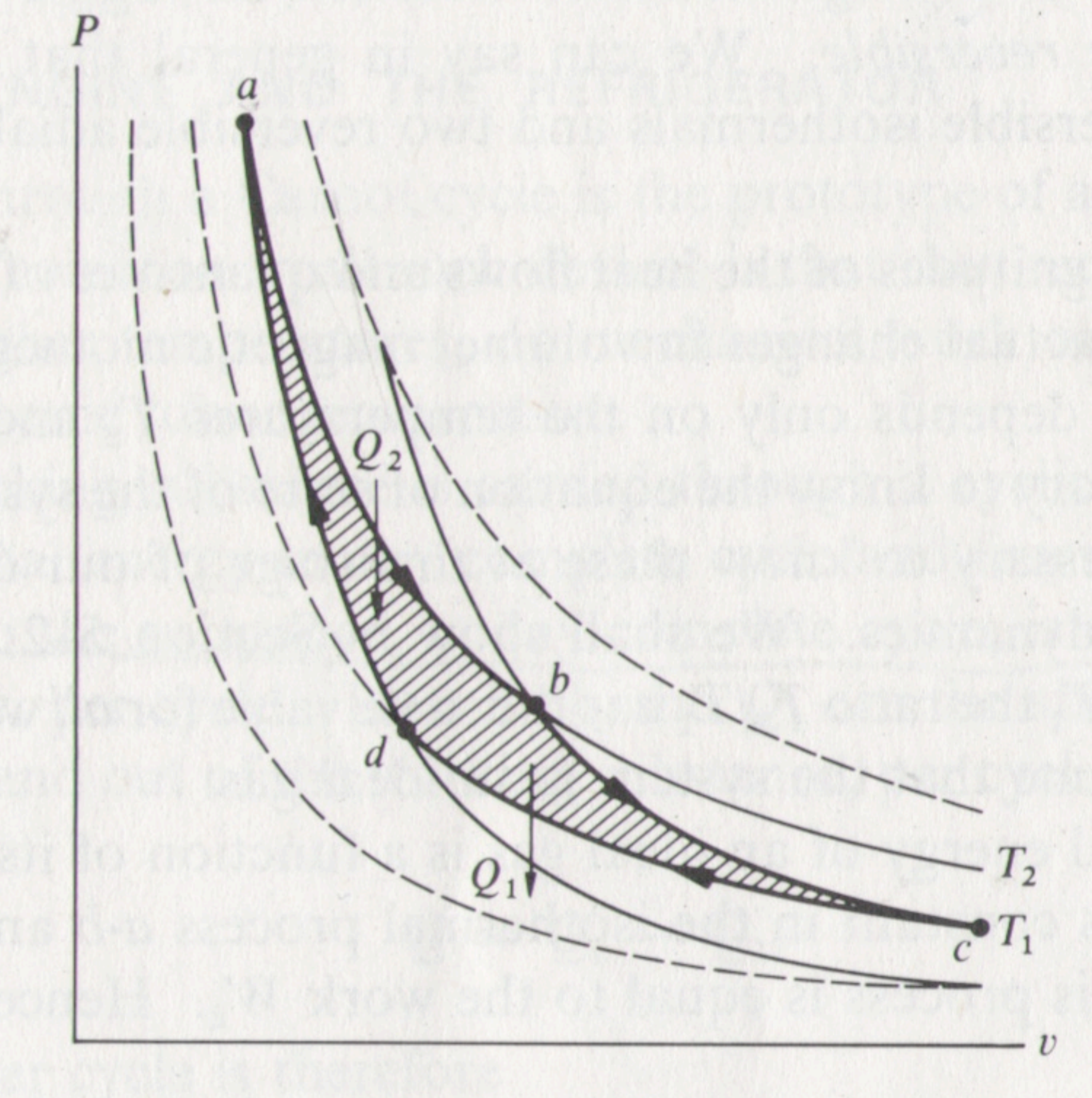


Fig. 4–6 The Carnot cycle.

a->b: reversible isothermal process

$$Q_2 = W_2 = nRT_2 \ln \frac{V_b}{V_a},$$

b->c: reversible adiabatic process

$$T_2 V_b^{\gamma-1} = T_1 V_c^{\gamma-1}$$

c->d: reversible isothermal process

$$Q_1 = W_1 = nRT_1 \ln \frac{V_c}{V_d}$$

d->a: reversible adiabatic process

$$T_2 V_a^{\gamma-1} = T_1 V_d^{\gamma-1}$$

$$\Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d} \quad \text{and} \quad \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

Heat engine

System in Carnot cycle is an example of cyclic heat engines

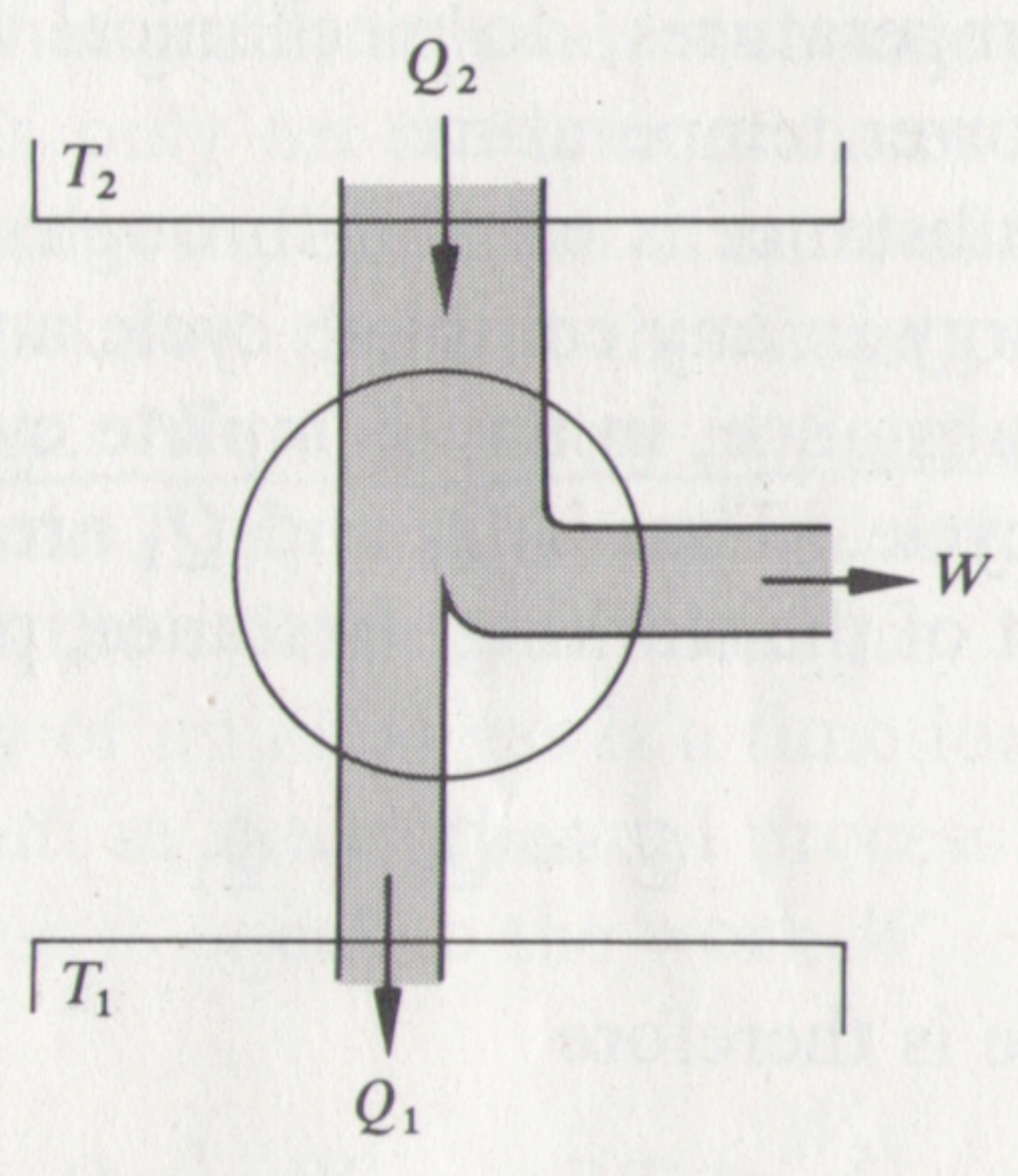


Fig. 4–7 Schematic flow diagram of a heat engine.

$$Q = Q_2 - Q_1$$

$$\Rightarrow \quad W = Q = Q_2 - Q_1$$

= net work per cycle

Thermal efficiency of a heat engine

$$\eta \equiv \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2}$$

For an ideal gas

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

$$\Rightarrow \quad \eta = 1 - \frac{T_1}{T_2}$$

Refrigerator

Inverse Carnot cycle is an example of cyclic heat pump or refrigerator

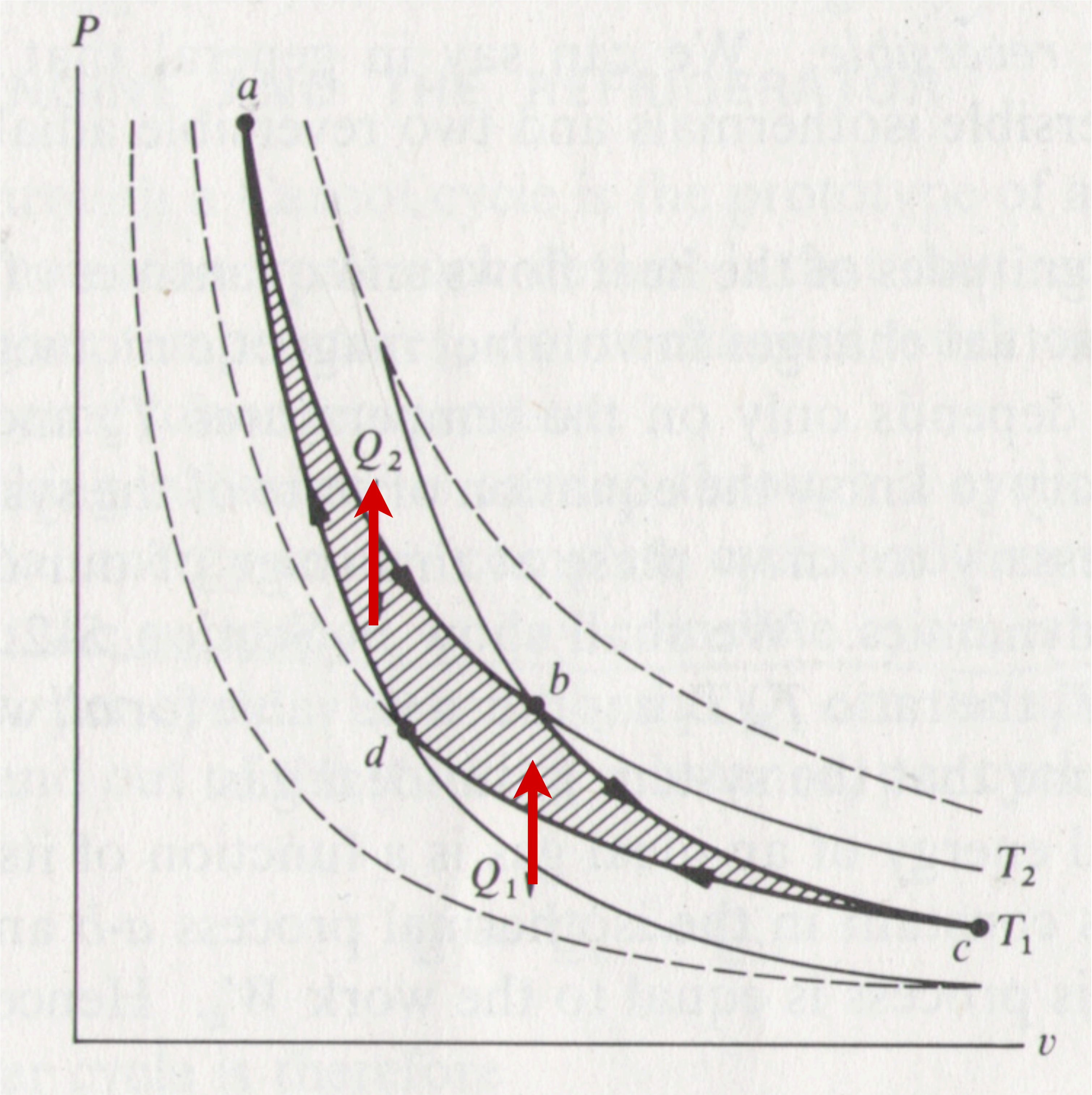


Fig. 4–6 The Carnot cycle.

a -> d -> c -> b

Coefficient of performance

$$c \equiv \frac{Q_1}{W} = \frac{Q_1}{Q_2 - Q_1}$$

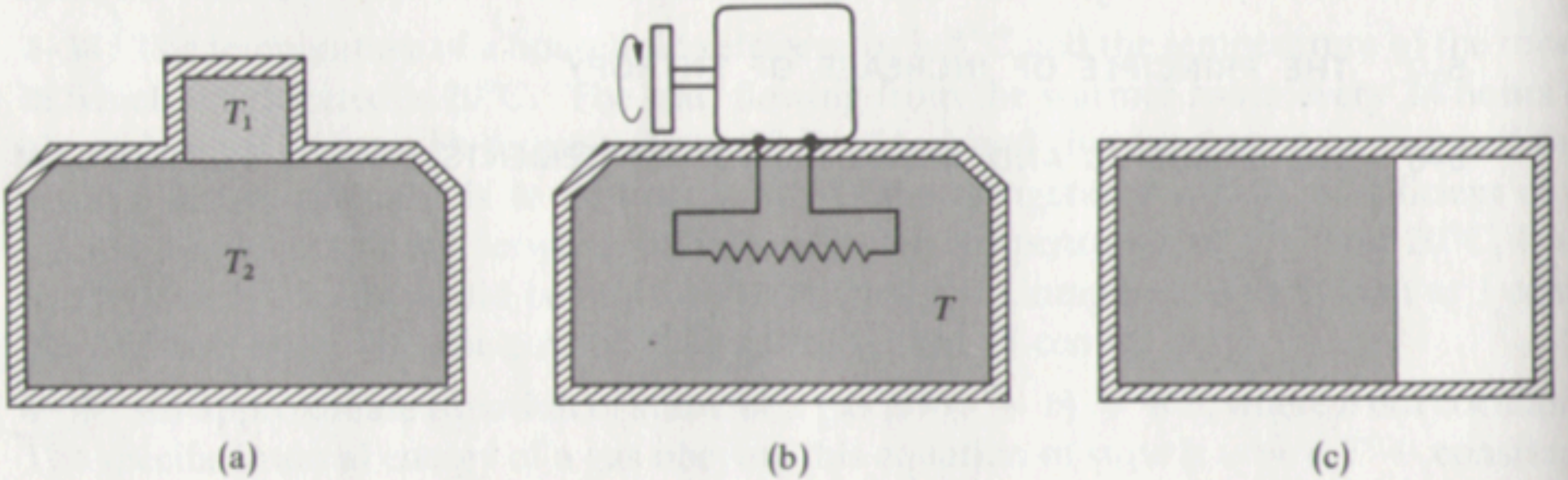
For an ideal gas

$$c = \frac{T_1}{T_2 - T_1}$$

Entropy and 2nd Law of thermodynamics

The 2nd law of thermodynamics

3 examples:



(a) (b) (c)

Fig. 5–1 In part (a) there is a reversible heat flow between a body at temperature T_1 and a large heat reservoir at a higher temperature T_2. In (b), a rotating flywheel drives a generator which sends a current through a resistor in a heat reservoir. In (c), a gas in the left portion of the container performs a free expansion into the evacuated region when the diaphragm is punctured.

Thermodynamic temperature

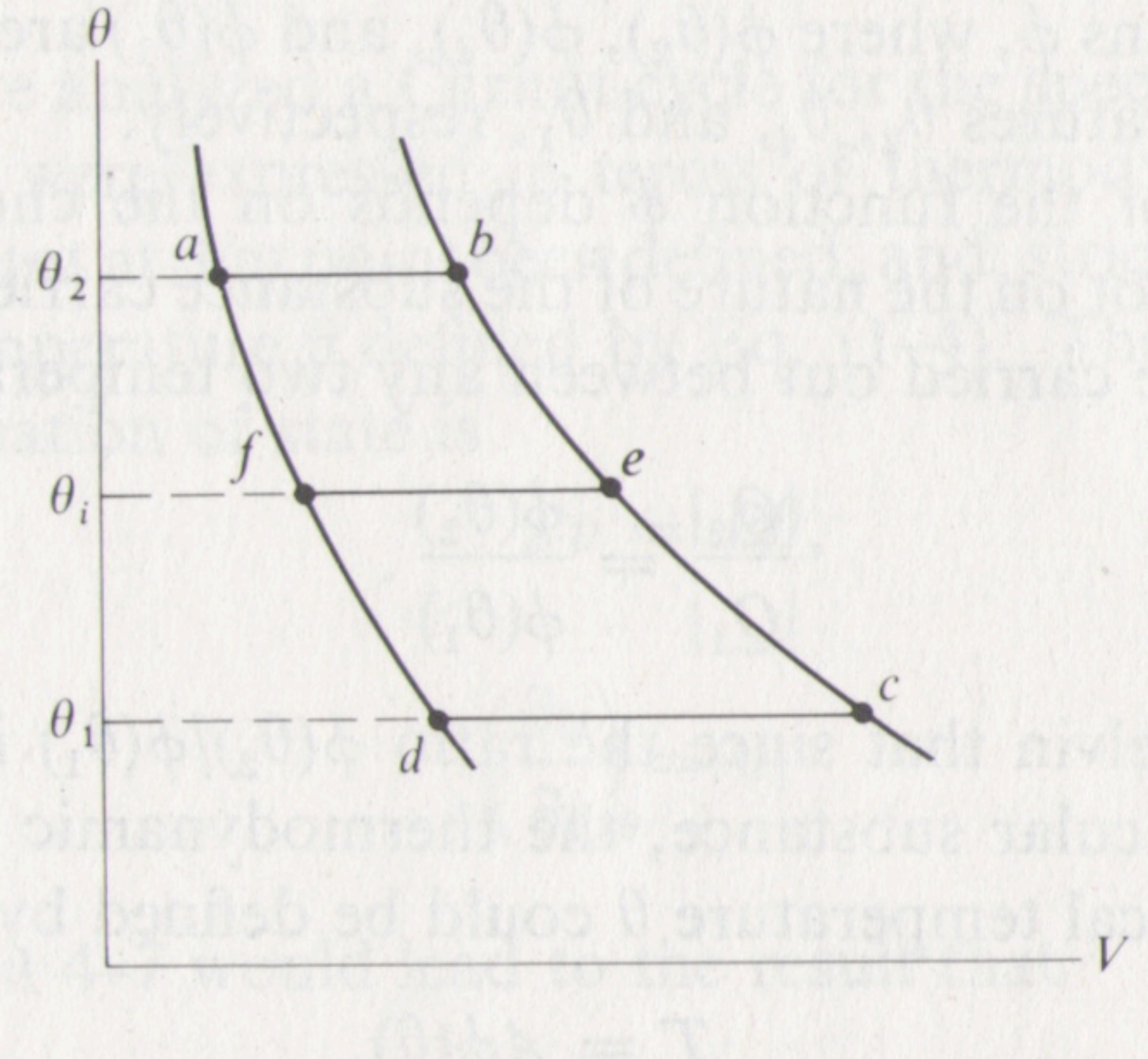


Fig. 5–2 Carnot cycles represented in the θ–V plane. Curves *a-f-d* and *b-e-c* are reversible adiabatics.

$$W = |Q_2| - |Q_1|$$

2nd law :

For any two θ_2 and θ_1,

the ratio $\dfrac{|Q_2|}{|Q_1|}$

in a Carnot cycle has

the same value

for all systems,

whatever their nature

$$\Rightarrow \quad \frac{|Q_2|}{|Q_1|} = f(\theta_2, \theta_1)$$

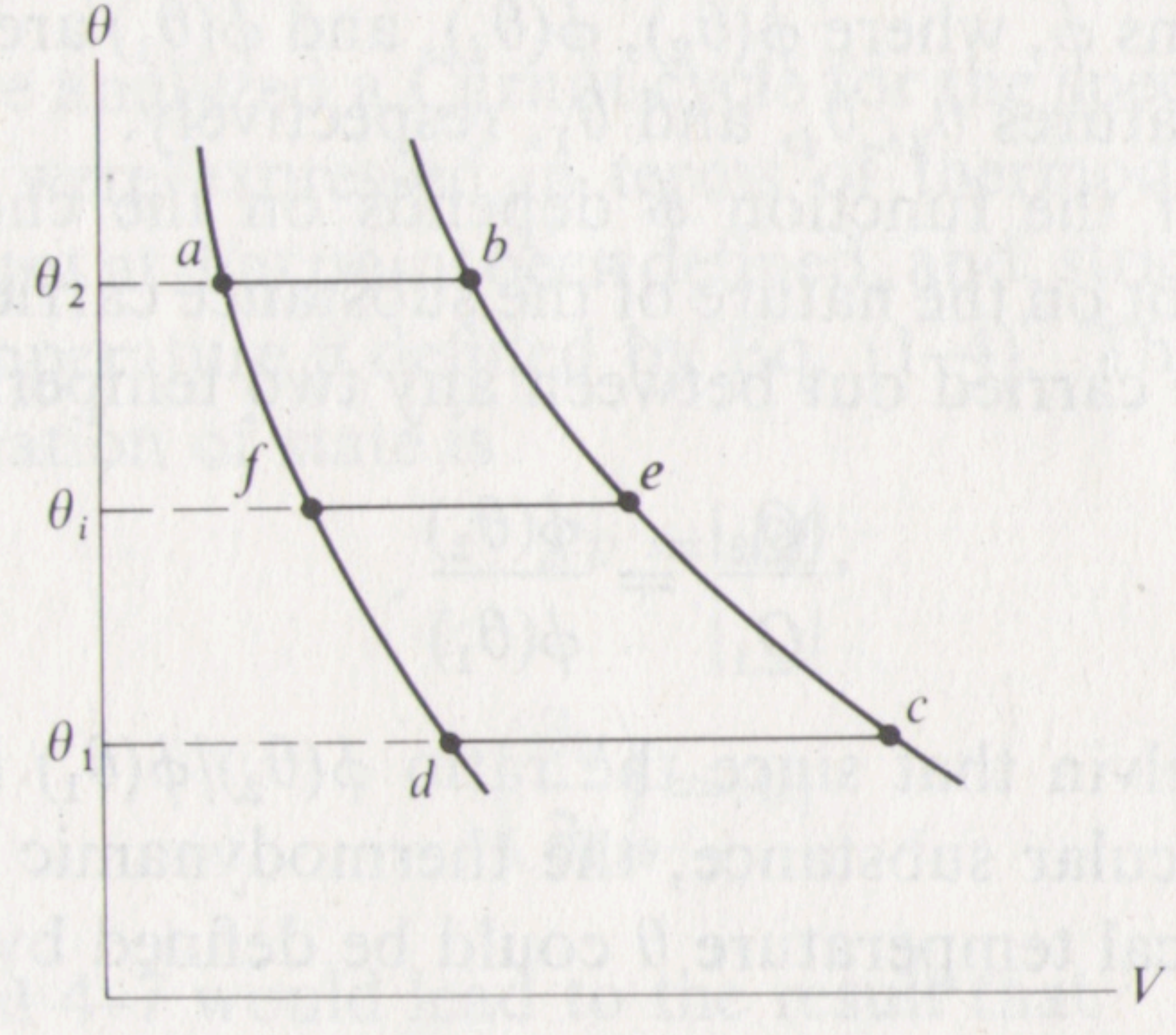


Fig. 5–2 Carnot cycles represented in the *θ–V* plane. Curves *a-f-d* and *b-e-c* are reversible adiabatics.

$$\frac{|Q_2|}{|Q_i|} = f(\theta_2, \theta_i)$$

$$\frac{|Q_i|}{|Q_1|} = f(\theta_i, \theta_1)$$

$$\Rightarrow \quad f(\theta_2, \theta_1) = \frac{|Q_2|}{|Q_1|}$$

$$= \frac{|Q_2|}{|Q_i|}\frac{|Q_i|}{|Q_1|}$$

$$= f(\theta_2, \theta_i) f(\theta_i, \theta_1)$$

$$\Rightarrow f(\theta_2, \theta_i) = \frac{\phi(\theta_2)}{\phi(\theta_1)}$$

Empirical and thermodynamic temperatures

Empirical temperature $\theta_{\text{gas}} = 273.16K \times \lim_{P_3 \to 0} \left(\frac{P_{\text{gas}}}{P_3} \right)_V$

$$\text{Strictly : for an ideal gas } Pv = R\theta \quad \text{and} \quad \left(\frac{\partial u}{\partial v} \right)_\theta = 0$$

$$\text{Kelvin :} \quad T = A\phi(\theta) \quad \Rightarrow \quad \frac{|Q_2|}{|Q_1|} = \frac{T_2}{T_1}$$

for whatever system is carried through the Carnot cycle between T_2 and T_1

From our analysis of Carnot cycle for an ideal gas

$$\frac{\theta_2}{\theta_1} = \frac{|Q_2|}{|Q_1|} = \frac{T_2}{T_1} \quad \Rightarrow \quad \theta \equiv T$$

Entropy

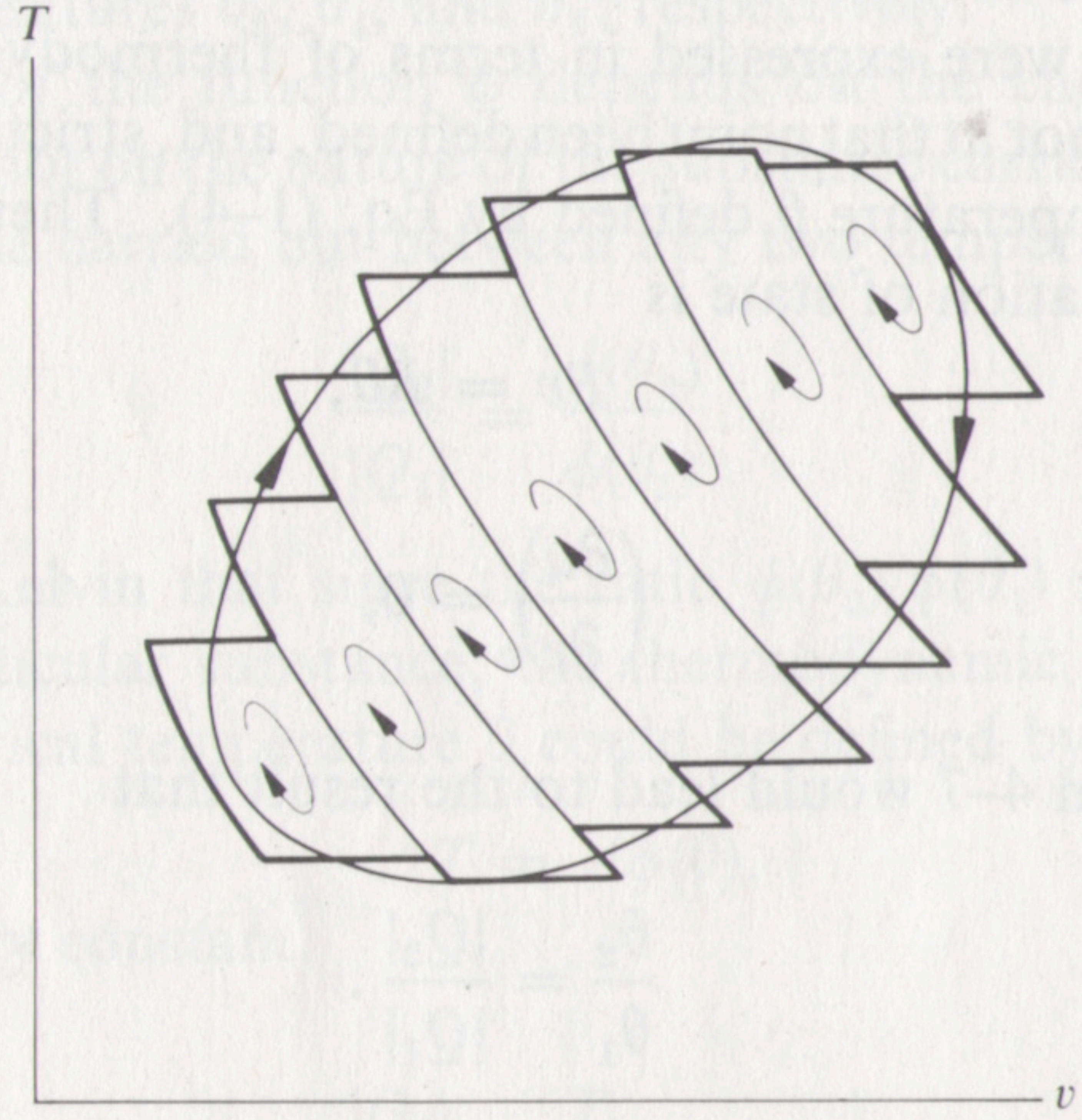


Fig. 5–3 Any arbitrary reversible cyclic process can be approximated by a number of small Carnot cycles.

For a Carnot cycle

$$\frac{T_2}{T_1} = -\frac{Q_2}{Q_1}$$

$$\Rightarrow \quad \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

$$\frac{\Delta Q_{\rm top}}{T_{\rm top}} + \frac{\Delta Q_{\rm bottom}}{T_{\rm bottom}} = 0$$

$$\Rightarrow \quad \sum \frac{\Delta Q_i}{T_i} = 0$$

$$\Rightarrow \quad \oint \frac{\delta Q}{T} = 0$$

S = Entropy

$$\oint \frac{\delta Q}{T} = 0 \quad \Rightarrow \quad \frac{\delta Q}{T} \text{ is an exact differential : } \quad dS \equiv \frac{\delta Q}{T}$$

$$\oint dS = 0 \quad \Rightarrow \quad S_b - S_a = \int_a^b dS \qquad \text{independent on path}$$

$$s \equiv \frac{S}{n} \qquad \text{specific entropy}$$

Later: it is possible to define an absolute scale of entropy

In quantum mechanics

$$Z = \sum_{\mathrm{n}} e^{-kE_n}, \quad \sum_n \equiv \text{ sum over quant. mech. states,} \quad \beta = \frac{1}{kT}$$

$$S = k\Big(\ln \mathcal{Z} - \beta\frac{\partial}{\partial\beta}\ln \mathcal{Z}\Big), \qquad k \equiv \text{ Boltzmann constant}$$

Entropy changes in reversible processes

For any adiabatic reversible process $\Delta S = \int dS = \int \frac{\delta Q}{T} = 0$

For a reversible isothermal process

$$S_b - S_a = \int_a^b \frac{\delta Q}{T} = \frac{1}{T}\int_a^b \delta Q = \frac{Q_{a\to b}}{T}$$

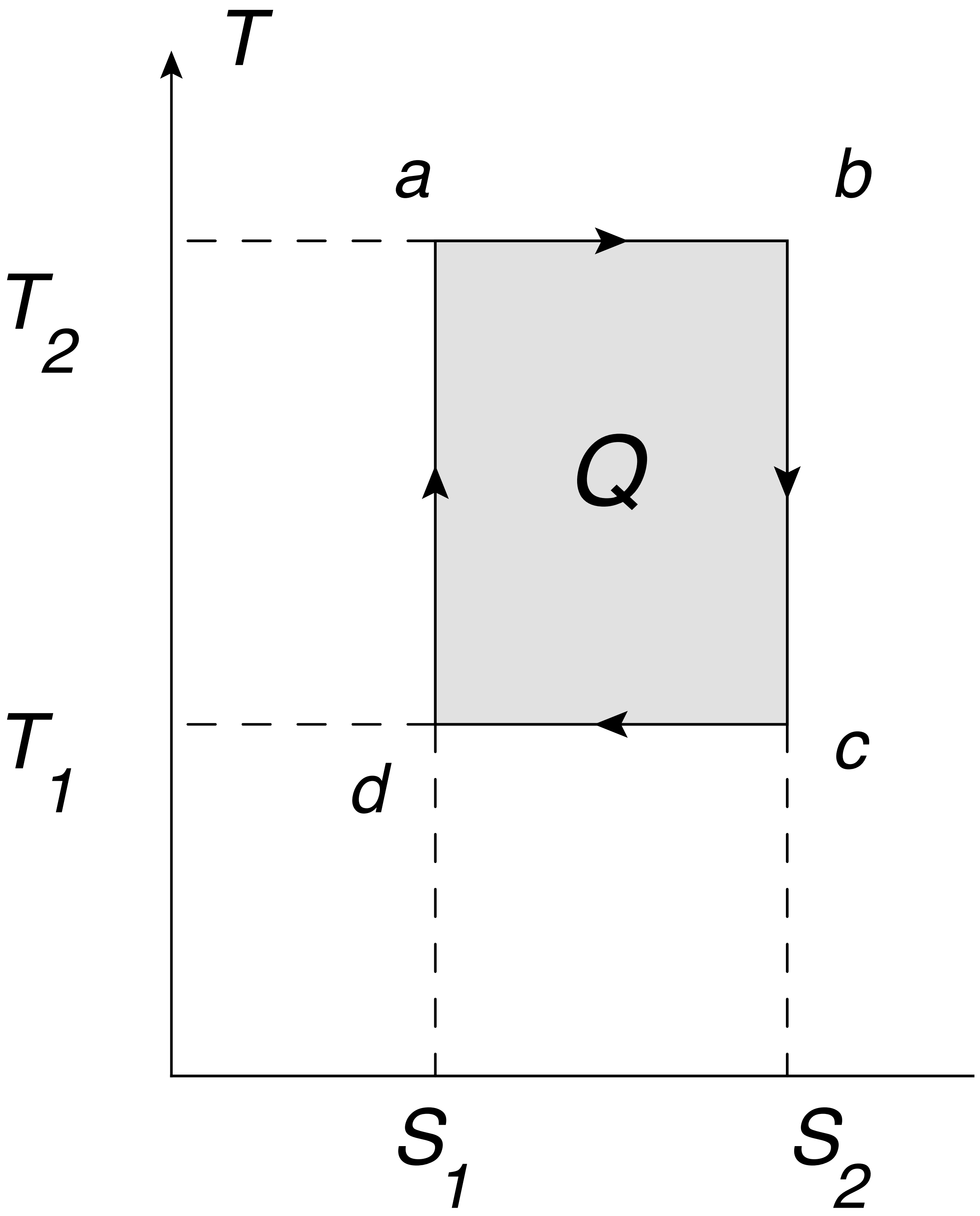
For a phase transition at constant P and T $s_2 - s_1 = \frac{l}{T}$

For a general process $S_b - S_a = \int_a^b \frac{\delta Q}{T}$

At constant volume $(s_b - s_a)_v = \int_{T_1}^{T_2} c_v \frac{dT}{T} = c_v \ln \frac{T_2}{T_1}$

At constant pressure $(s_b - s_a)_P = \int_{T_1}^{T_2} c_P \frac{dT}{T} = c_P \ln \frac{T_2}{T_1}$

Temperature-entropy diagrams



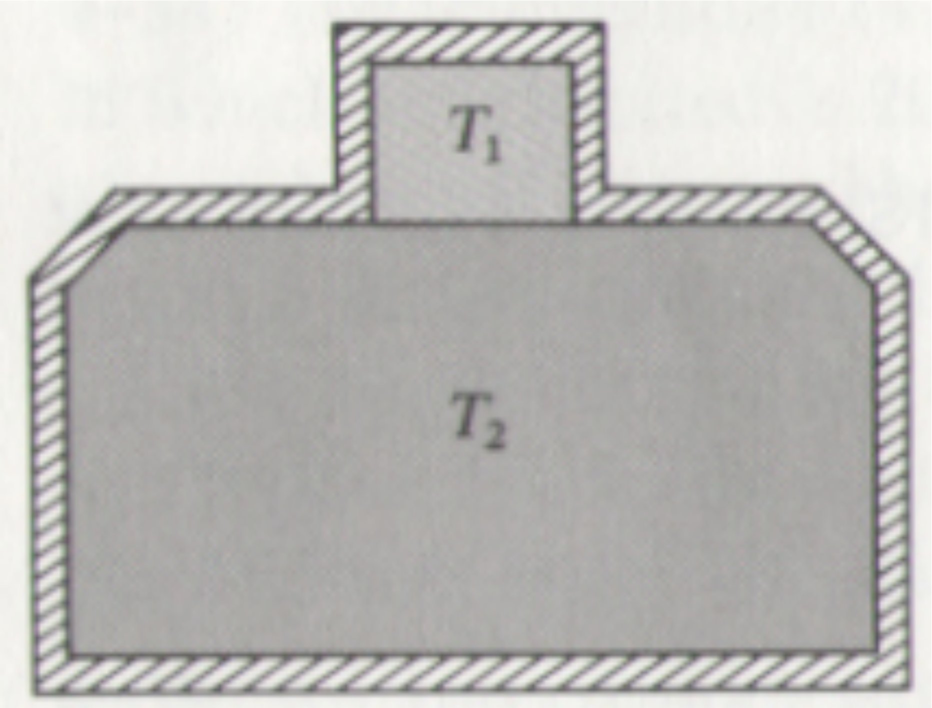
$$\oint T dS \; =$$

$$\int_a^b \delta Q - \int_d^c \delta Q \; = \; Q$$

$(Q \equiv \text{net heat flow})$

In a cyclic reversible process heat flow = area enclosed by T-S diagram

Entropy changes in irreversible processes



Entropy is a function of state
=> change of entropy is the same
whether the process is reversible
or irreversible

In a reversible process
at constant pressure

$$\Delta S_{\text{body}} = C_P \ln \frac{T_2}{T_1}$$

$$\text{Heat flow into the body}: \; Q = C_P(T_2 - T_1)$$

Change of reservoir entropy is the same as in isothermal process

$$\Delta S_{\text{reservoir}} = -\frac{Q}{T_2} = -C_P \frac{T_2 - T_1}{T_2}$$

$$\Delta S = \Delta S_{\text{body}} + \Delta S_{\text{reservoir}} = C_P\left(\ln\frac{T_2}{T_1} - \frac{T_2 - T_1}{T_2}\right)$$

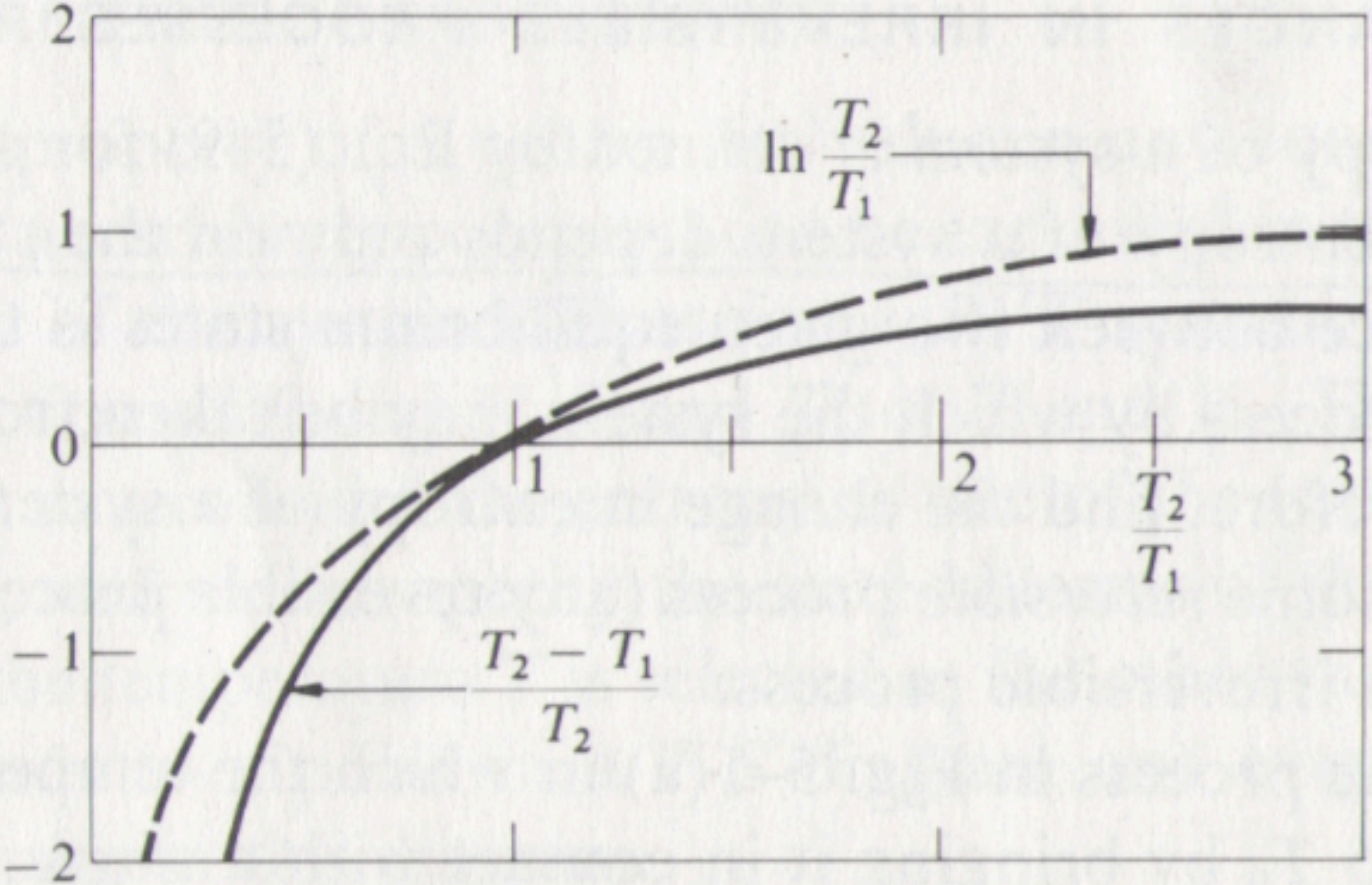


Fig. 5–5 A graph of ln (T_2/T_1) and $(T_2 - T_1)/T_1$ as a function of T_2/T_1.

Law of increasing entropy:

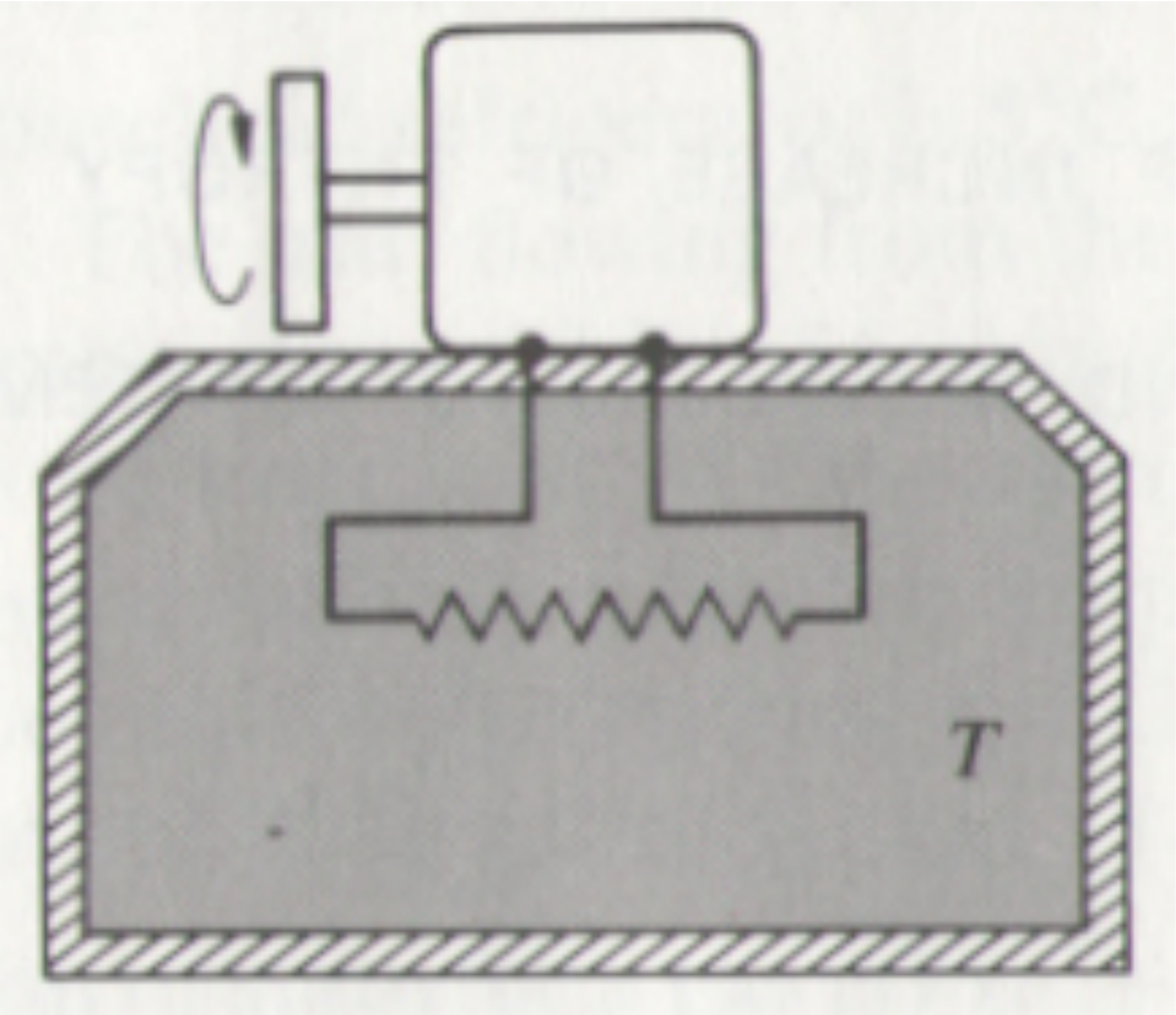
$$\underline{\Delta S \geq 0}$$

(= for reversible processes)

Heat flow Q => entropy of the reservoir increases by Q/T

Temperature of resistor constant => no change of properties of the resistor => no change of entropy of the resistor =>

$$\Delta S_{\text{reservoir}} + \Delta S_{\text{resistor}} = \Delta S > 0$$



Entropy increase of the resistor as a result of dissipative work balances the entropy decrease due to the heat flow out of the resistor

Clausius form of the 2nd law

There exists no thermodynamic transformation whose sole effect is to extract a quantity of heat from a colder reservoir and to deliver it to a hotter reservoir.

$$A@T_1 \overset{Q}{\to} B@T_2 \quad \Rightarrow$$

$$\Delta S_A = -\frac{Q}{T_1}, \qquad \Delta S_B = \frac{Q}{T_2}$$

$$T_2 > T_1 \ \& \ Q > 0 \quad \Rightarrow \quad \Delta S < 0$$

Kelvin-Planck form of the 2nd law

There exists no thermodynamic transformation whose sole effect is to extract a quantity of heat from a given heat reservoir and to convert it entirely into work.

These two formulations of the 2nd law are equivalent.
To prove this, we will demonstrate that
if Kelvin Statement (``$\mathcal{K}$'') is false then the
Clausius Statement (``$\mathcal{C}$'') is false, and vice versa.

Proof Clausius form <=> Kelvin-Planck form

Proof that ($\mathcal{K}$ false) => ($\mathcal{C}$ false)

If we can take heat from a reservoir at lower temperature T1 and convert it into work, we can then convert this work into heat (work can be always converted into heat!) at higher temperature T2 > T1. Hence, $\mathcal{C}$ will be false.

Proof that ($\mathcal{C}$ false) => ($\mathcal{K}$ false)

Suppose that the system undergoes a cyclic transformation (and it works in the following way):

1. Absorbs heat Q_2 from reservoir T_2;
2. Rejects heat $Q_1 > 0$ into reservoir T_1;
3. Performs work $W > 0$.

If $\mathcal{C}$ is false, we can take Q2 from reservoir T1 and deliver it to reservoir T2 > T1. Let the system operate one cycle, so that the heat extracted from T2 is exactly Q2.

The result is that the total heat extracted from T1 (which is Q2 − Q1)

is entirely converted into work $\Rightarrow$ $\mathcal{K}$ is false.

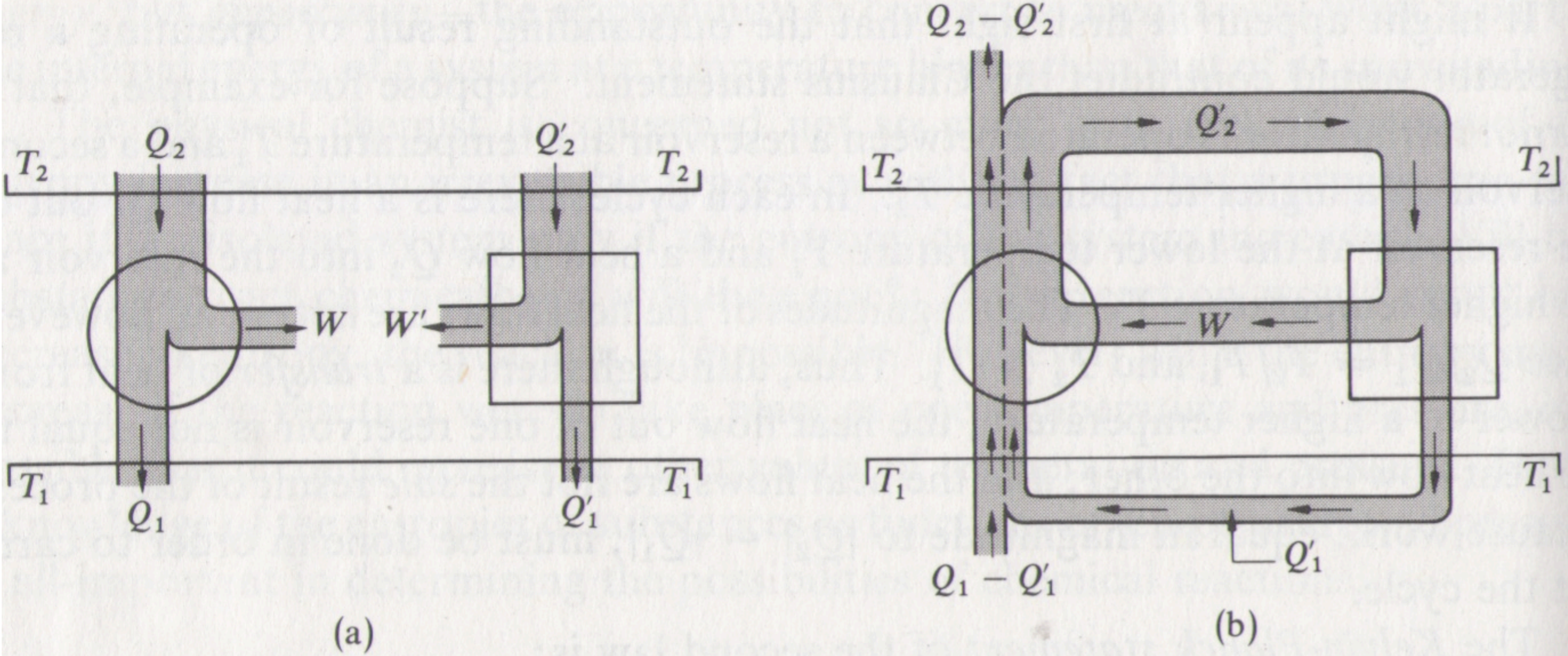


Fig. 5–6 In part (a), the circle represents a Carnot engine and the rectangle an assumed engine having a higher thermal efficiency. If the assumed engine were to drive the Carnot engine in reverse as a refrigerator, as in part (b), the result would violate the Clausius statement of the second law.

The sole result is the transfer from low- to high-temperature reservoir (represented by width of the left part of the pipeline) => contradicts Clausius statement.

=> No engine operating between two reservoirs at given temperatures can have a higher efficiency than the Carnot engine operating between same reservoirs

Combined first and second laws

$$\left.\begin{array}{rcl} \delta Q & = & du + \delta W \\ \delta Q & = & TdS \\ \delta W & = & PdV \end{array}\right\} \Rightarrow \quad TdS \;=\; dU + PdV$$

NB: the two last equations at the left are true only for reversible processes, but the right equation is not restricted to a process at all, it is correct for any two equilibrium states

However, if the process is irreversible, $TdS \neq \delta Q$ and $\delta W \neq PdV$

Example: stirring work done on adiabatic system kept at constant volume.

$$TdS > 0, \quad \text{but} \quad \delta Q = 0 \text{ and } PdV = 0$$

Goal:
Derive three TdS equations

$$\begin{aligned} TdS &= c_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv \\ TdS &= c_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP \\ TdS &= c_P\left(\frac{\partial T}{\partial v}\right)_P dv + c_v\left(\frac{\partial T}{\partial P}\right)_v dP \end{aligned}$$

and

Put all partial derivatives in the standard form

$\Leftrightarrow$ express them in terms of c_P, β, and κ

(in addition to P, V, and T)

T and *v* as independent variables

$$\left.\begin{aligned} ds &= \tfrac{1}{T}(du + Pdv) \\ du &= \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \end{aligned}\right\} \Rightarrow$$

$$\Rightarrow \quad ds = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v dT + \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv$$

Since S is a function of state $ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$

$$\Rightarrow \quad \left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v = \frac{c_v}{T}, \qquad \left(\frac{\partial s}{\partial v}\right)_T = \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]$$

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial s}{\partial T}\right)_v\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial v}\right)_T\right]_v = \frac{\partial^2 s}{\partial v \partial T}$$

$$\Rightarrow \quad \frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} = \frac{1}{T}\left[\frac{\partial^2 u}{\partial v \partial T} + \left(\frac{\partial P}{\partial T}\right)_v\right] - \frac{1}{T^2}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]$$

$$\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial v}\right)_T = -\frac{\beta}{\kappa}$$

$$\Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P = \frac{\beta}{\kappa}T - P$$

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T} \quad \Rightarrow \quad ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv = \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$\Rightarrow \quad Tds = c_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv$$

$$T\frac{\partial P(v,T)}{\partial T} = \left(\frac{\partial u}{\partial v}\right)_T + P \overset{\partial/\partial T}{\Rightarrow} T\frac{\partial^2 P(v,T)}{\partial T^2} + \frac{\partial P(v,T)}{\partial T}$$

$$= \frac{\partial^2 u(v,T)}{\partial v \partial T} + \frac{\partial P(v,T)}{\partial T} \Rightarrow \left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v$$

For He^4 $\left(\frac{\partial c_v}{\partial v}\right)_T = \left(\frac{\partial c_v}{\partial \rho_r}\right)_T \left(\frac{\partial \rho_r}{\partial v}\right)_T = \left(\frac{\partial c_v}{\partial \rho_r}\right)_T \frac{\rho_r^2}{0.0582} = 1.7 \times 10^5 \frac{J}{m^3 K}$

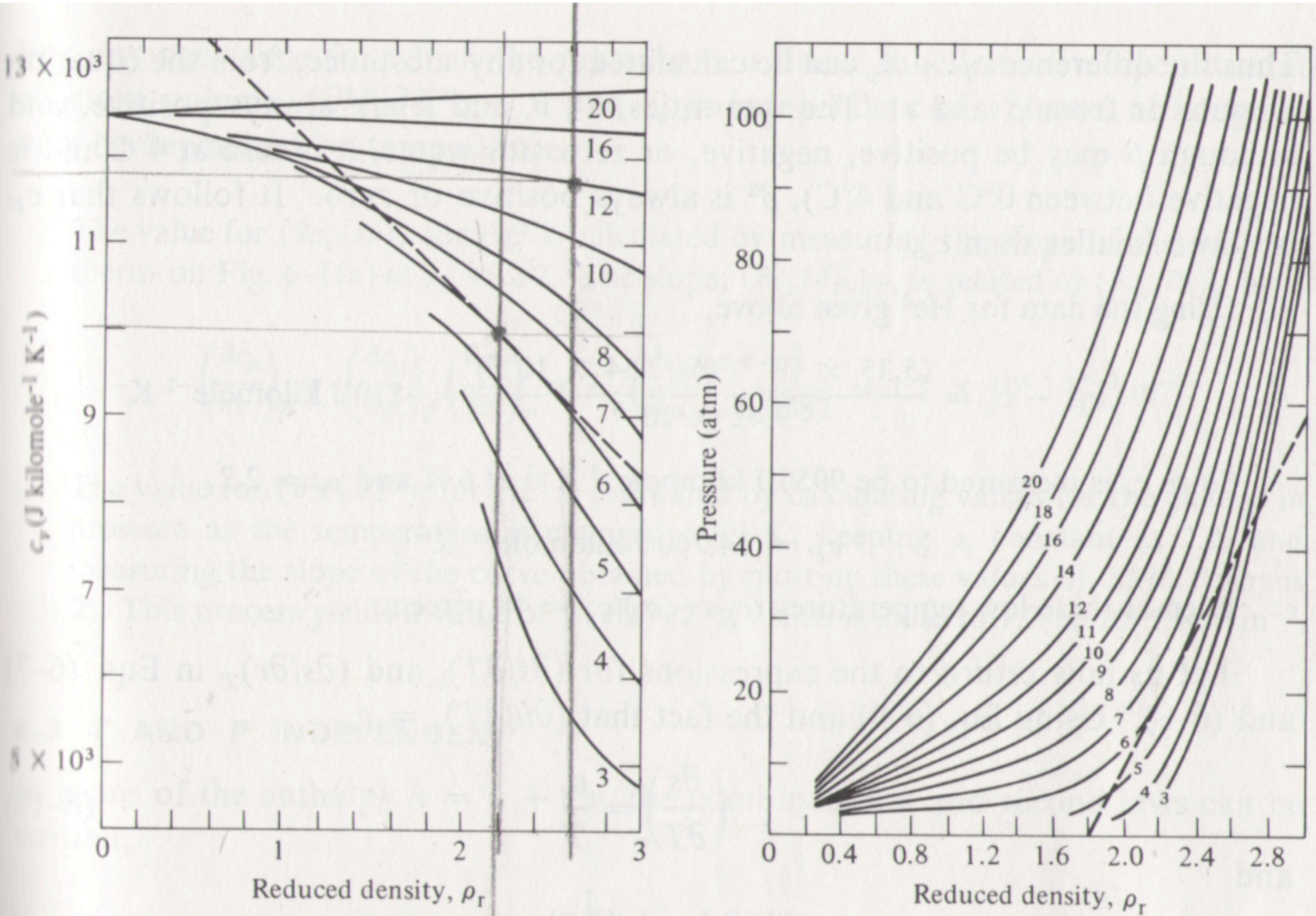


Fig. 6–1 (a) The specific heat capacity at constant volume and (b) the pressure of He^4 as a function of reduced density at temperatures between 3 and 20 K. Each curve is marked with the temperature in kelvins. The reduced density ρ_r is the ratio of the actual density of He^4 to 68.8 kg m^{-3}. The dashed lines are the tangents to the 6 K isotherm at $\rho_r = 2.2$. The experiments were performed by Hill and Lounasmaa. (These figures are reprinted by permission from O. V. Lounasmaa's article, "The Thermodynamic Properties of Fluid Helium, *Philosophical Transactions of the Royal Society of London* 252A (1960): 357 (Figs. 4 and 7).)

$$\frac{1}{T}\frac{\partial^2 u}{\partial v\partial T} = \frac{1}{T}\Big[\frac{\partial^2 u}{\partial v\partial T} + \Big(\frac{\partial P}{\partial T}\Big)_v\Big] - \frac{1}{T^2}\Big[\Big(\frac{\partial u}{\partial v}\Big)_T + P\Big]$$

$$\Rightarrow \quad \Big(\frac{\partial u}{\partial v}\Big)_T = T\Big(\frac{\partial P}{\partial T}\Big)_v - P = \frac{T\beta}{\kappa} - P$$

$$du = \Big(\frac{\partial u}{\partial T}\Big)_v dT + \Big(\frac{\partial u}{\partial v}\Big)_T dv \quad \Rightarrow \quad du = c_v dT + \Big[T\Big(\frac{\partial P}{\partial T}\Big)_v - P\Big]dv$$

From the 1st law : $c_P - c_v = \Big[\Big(\frac{\partial u}{\partial v}\Big)_T + P\Big]\Big(\frac{dv}{dT}\Big)_P.$

Math formula : $\Big(\frac{\partial P}{\partial T}\Big)_v = -\Big(\frac{\partial v}{\partial T}\Big)_P\Big(\frac{\partial P}{\partial v}\Big)_T$

$$\Rightarrow \quad c_P - c_v = T\Big(\frac{\partial P}{\partial T}\Big)_v\Big(\frac{\partial v}{\partial T}\Big)_P = \Big\{\frac{1}{v^2}\Big(\frac{\partial v}{\partial T}\Big)_P^2 Tv\Big\}\Big\{-v\Big(\frac{\partial P}{\partial v}\Big)_T\Big\}$$

$$\Rightarrow \quad c_P - c_v = \frac{\beta^2 Tv}{\kappa}$$

From the He^4 data $c_v = 9950\ \mathrm{J(kmol)^{-1}K^{-1}}$, $c_P = 14760\ \mathrm{J(kmol)^{-1}K^{-1}}$

T and *P* as independent variables

$$h = u + Pv \quad \Rightarrow \quad ds = \frac{1}{T}(dh - v dP)$$

$$dh = \left(\tfrac{\partial h}{\partial T}\right)_P dT + \left(\tfrac{\partial h}{\partial P}\right)_T dP \quad \Rightarrow \quad \begin{aligned} ds &= \tfrac{1}{T}\left(\tfrac{\partial h}{\partial T}\right)_P dT + \tfrac{1}{T}\left[\left(\tfrac{\partial h}{\partial P}\right)_T - v\right] dP \\ ds &= \left(\tfrac{\partial s}{\partial T}\right)_P dT + \left(\tfrac{\partial s}{\partial P}\right)_T dP \end{aligned}$$

$$\Rightarrow \quad \left(\frac{\partial s}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_P, \qquad \left(\frac{\partial s}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right]$$

$$\begin{aligned} \frac{\partial^2 s}{\partial P \partial T} &= \frac{\partial}{\partial P}\left(\frac{\partial s}{\partial T}\right)_P = \frac{\partial}{\partial P}\frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_P = \frac{1}{T}\frac{\partial^2 h}{\partial T \partial P}, \\ \frac{\partial^2 s}{\partial P \partial T} &= \frac{\partial}{\partial T}\left(\frac{\partial s}{\partial P}\right)_T = \frac{\partial}{\partial T}\frac{1}{T}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] \\ &= -\frac{1}{T^2}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] + \frac{1}{T}\frac{\partial^2 h}{\partial T \partial P} - \frac{1}{T}\left(\frac{\partial v}{\partial T}\right)_P \\ \Rightarrow \left(\frac{\partial h}{\partial P}\right)_T &= -T\left(\frac{\partial v}{\partial T}\right)_P + v = -\beta v T + v \end{aligned}$$

$$
\begin{aligned}
c_P &= \left(\frac{\partial h}{\partial T}\right)_P \\
\Rightarrow \quad dh &= c_P dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP \quad \Rightarrow \quad \left(\frac{\partial h}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P \\
\left(\frac{\partial s}{\partial T}\right)_P &= \frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_P, \qquad \left(\frac{\partial s}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] \\
\Rightarrow \quad \left(\frac{\partial s}{\partial T}\right)_P &= \frac{c_P}{T}, \qquad \left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P
\end{aligned}
$$

$$
\begin{aligned}
TdS &= \quad = T\left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial P}\right)_T dP = c_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP \quad \Rightarrow \\
\left(\frac{\partial c_P}{\partial P}\right)_T &= \left(\frac{\partial^2 h}{\partial T \partial P}\right) = \frac{\partial}{\partial T}\left(\frac{\partial h}{\partial P}\right)_T = \left(\frac{\partial v}{\partial T}\right)_P - \frac{\partial}{\partial T} T\left(\frac{\partial v}{\partial T}\right)_P = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P
\end{aligned}
$$

$$
\Rightarrow \quad \left(\frac{\partial c_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P
$$

P and *v* as independent variables

We will prove

$$\left(\frac{\partial s}{\partial P}\right)_v = \frac{c_v \kappa}{T\beta}$$
$$\left(\frac{\partial s}{\partial v}\right)_P = \frac{c_P}{Tv\beta}$$

$$ds = \left(\frac{\partial s}{\partial v}\right)_P dv + \left(\frac{\partial s}{\partial P}\right)_v dP$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv, \qquad dT = \left(\frac{\partial T}{\partial P}\right)_v dP + \left(\frac{\partial T}{\partial v}\right)_P dv$$

$$\Rightarrow \quad ds = \left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial T}{\partial P}\right)_v dP + \left[\left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_P + \left(\frac{\partial s}{\partial v}\right)_T\right] dv$$

$(*)$

$$\begin{aligned}
\left(\frac{\partial s}{\partial T}\right)_v &= \frac{c_v}{T} \quad\Rightarrow\quad \left(\frac{\partial s}{\partial P}\right)_v = \left(\frac{\partial s}{\partial T}\right)_v\left(\frac{\partial T}{\partial P}\right)_v = \frac{c_v}{T}\left(\frac{\partial T}{\partial P}\right)_v, \\
c_P - c_v &= T\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_P \quad\Rightarrow \\
\left(\frac{\partial s}{\partial v}\right)_P &= \left[\left(\frac{\partial s}{\partial T}\right)_v\left(\frac{\partial T}{\partial v}\right)_P + \left(\frac{\partial s}{\partial v}\right)_T\right] \\
&= \left[\frac{c_v}{T}\left(\frac{\partial T}{\partial v}\right)_P + \left(\frac{\partial P}{\partial T}\right)_v\right] = \frac{c_P}{T}\left(\frac{\partial T}{\partial v}\right)_P
\end{aligned}$$

$$\left.\begin{aligned}
\left(\frac{\partial s}{\partial v}\right)_T &= \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] \\
\left(\frac{\partial u}{\partial v}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_v - P
\end{aligned}\right\} \Rightarrow \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\left.\begin{aligned}
\left(\frac{\partial T}{\partial P}\right)_v &= \frac{1}{\left(\partial P/\partial T\right)_v} = -\left(\frac{\partial T}{\partial v}\right)_P\left(\frac{\partial v}{\partial P}\right)_T = \frac{\kappa}{\beta} \\
\left(\frac{\partial T}{\partial v}\right)_P &= \frac{1}{\left(\partial v/\partial T\right)_P} = \frac{1}{v\beta}
\end{aligned}\right\} \Rightarrow \quad \begin{aligned}
\left(\frac{\partial s}{\partial P}\right)_v &= \frac{c_v\kappa}{T\beta} \\
\left(\frac{\partial s}{\partial v}\right)_P &= \frac{c_P}{Tv\beta}
\end{aligned}$$

From the above equations and eqn. $(*)$

$$\Rightarrow \quad TdS = c_P\left(\frac{\partial T}{\partial v}\right)_P dv + c_v\left(\frac{\partial T}{\partial P}\right)_v dP$$

TdS equations

$$
\begin{aligned}
TdS &= c_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv \\
TdS &= c_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP \\
TdS &= c_P\left(\frac{\partial T}{\partial v}\right)_P dv + c_v\left(\frac{\partial T}{\partial P}\right)_v dP
\end{aligned}
$$

Examples:

Increase of temperature of solid or liquid under adiabatic compression

$$dq = Tds = 0 \quad \Rightarrow \quad c_v dT_s + \frac{\beta T}{\kappa} dv_s \quad \Rightarrow \quad dT_s = -\frac{\beta T}{\kappa c_v} dv_s$$

If the increase of pressure (rather than of volume) is specified

$$0 = Tds = c_P dT_s - \beta v T dP_s \quad \Rightarrow \quad dT_s = \frac{\beta v T}{\kappa c_P} dP_s$$

If b is positive, T increases when the pressure is applied => if it is desired to keep T=const, there must be a heat flow out of the system.

This heat flow can be found from $TdS = c_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$

$$\Rightarrow \quad \delta q_T = TdS = -T\left(\frac{\partial v}{\partial T}\right)_P dP = -\beta v T dP_T$$

The pressure needed to decrease the volume of the substance adiabatically can be found from

$$TdS = c_P\left(\frac{\partial T}{\partial v}\right)_P dv + c_v\left(\frac{\partial T}{\partial P}\right)_v dP$$

$$\Rightarrow \; TdS = 0 = \tfrac{\kappa c_v}{\beta} dP_s + \tfrac{c_P}{\beta v} dv_s \;\Rightarrow\; -\tfrac{1}{v}\left(\frac{\partial v}{\partial P}\right)_S = \kappa \tfrac{c_v}{c_P}$$

The compressibility κ is the isothermal compressibility $\kappa = \frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$.

$-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_S$ defines the adiabatic compressibility $\kappa_s \;\Rightarrow\; \kappa_s = \frac{\kappa}{\gamma}, \quad \gamma \equiv \frac{c_P}{c_v}$

Properties of a pure substance

$$\left.\begin{aligned} ds &= \tfrac{c_P}{T}dT - \left(\tfrac{\partial v}{\partial T}\right)_P dP, \\ dh &= c_P dT + \left[v - T\left(\tfrac{\partial v}{\partial T}\right)_P\right]dP \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} s &= s_0 + \int_{T_0}^{T} dT\ \tfrac{c_P}{T} - \int_{P_0}^{P} dP\ \left(\tfrac{\partial v}{\partial T}\right)_P, \\ h &= h_0 + \int_{T_0}^{T} dT\ c_P + \int_{P_0}^{P} dP\ \left[v - T\left(\tfrac{\partial v}{\partial T}\right)_P\right] \end{aligned}\right.$$

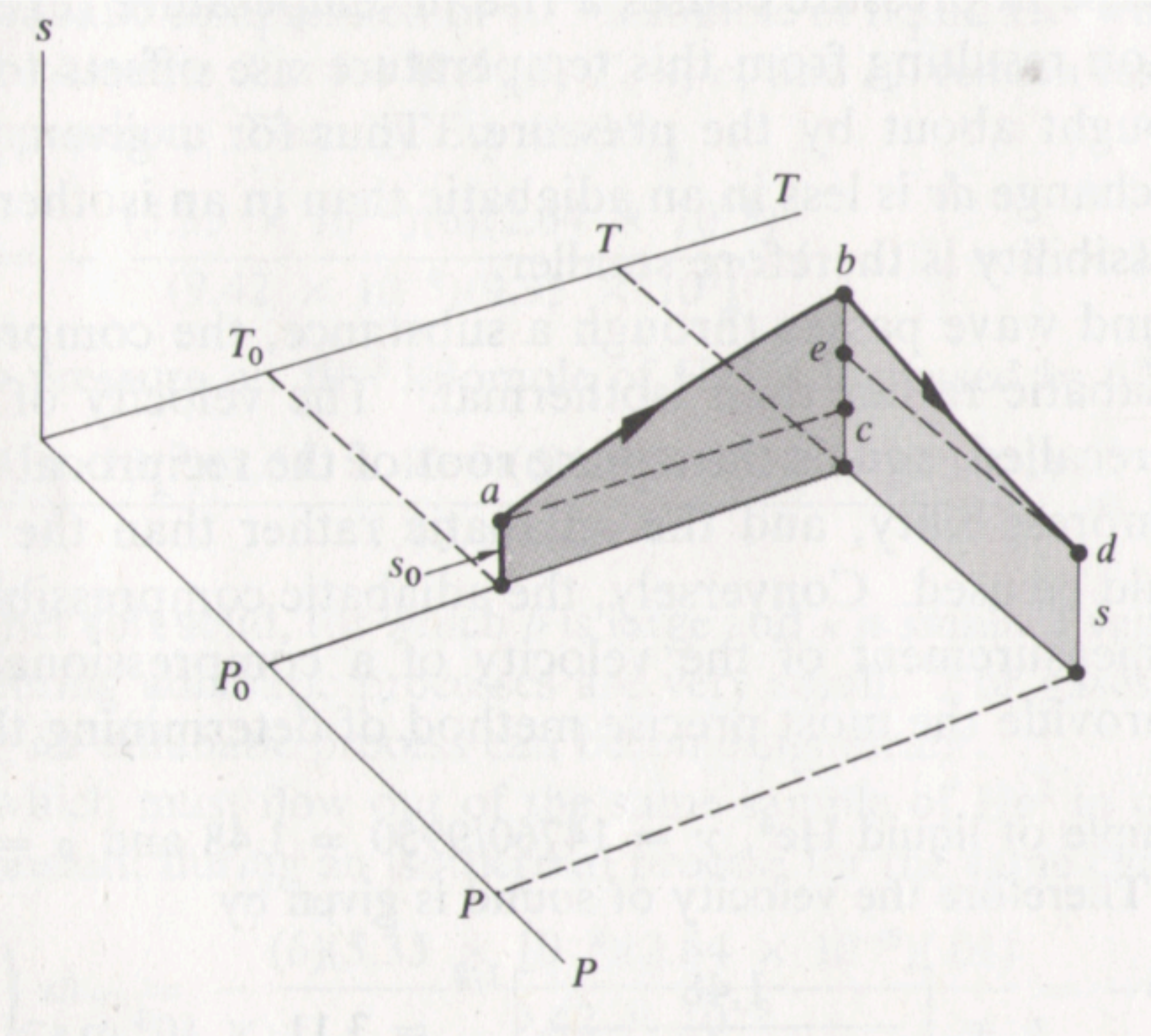


Fig. 6–2 Integration paths used in evaluation of entropy.

First integral: along a->b

Second integral: along b->d

If c_P is available at pressure P different from P_0,

$$c_{P_0} = c_P + T\int_{P_0}^{P}\left(\frac{\partial^2 v}{\partial T^2}\right)_P dP$$

$\Rightarrow$ Entropy and enthalpy can be determined from equation of state and $c_P(T)$

Properties of an ideal gas

$$\left.\begin{array}{l} \text{For an ideal gas} \quad v = \frac{RT}{P}, \quad \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}, \quad \left(\frac{\partial^2 v}{\partial T^2}\right)_P = 0 \\[2ex] c_{P_0} \;=\; c_P + T\int_{P_0}^{P}\left(\frac{\partial^2 v}{\partial T^2}\right)_P dP \quad\Rightarrow\quad c_P(T,\cancel{P}) = c_P(T) \end{array}\right\} \quad\Rightarrow$$

$$\Rightarrow \quad s \;=\; s_0 + \int_{T_0}^{T} dT\,\frac{c_P}{T} - R\ln\frac{P}{P_0}, \qquad h \;=\; h_0 + \int_{T_0}^{T} dT\, c_P$$

If $c_P = \text{const}$ $\quad\Rightarrow\quad$ $s \;=\; s_0 + c_P \ln\frac{T}{T_0} - R\ln\frac{P}{P_0}, \qquad h \;=\; h_0 + c_P(T - T_0)$

For an ideal gas $c_P = c_v + R \quad\Rightarrow$

$$s \;=\; s_0 + c_v \ln\frac{T}{T_0} + R\ln\frac{v}{v_0} \;=\; s_0 + c_v\ln\frac{P}{P_0} + c_P\ln\frac{v}{v_0}$$

For a reversible adiabatic process this gives $\left(\gamma \equiv \frac{c_P}{c_v}\right)$

$$c_v \ln P + c_P \ln v \;=\; \text{const} \quad\Rightarrow\quad P v^{\gamma} \;=\; \text{const}$$

Properties of a van der Waals gas

It is convenient to choose T and v as independent variables

$$\text{Entropy}: \quad s = s_0 + \int_{T_0}^{T} dT\, \frac{c_v}{T} + \int_{v_0}^{v} dv\, \left(\frac{\partial P}{\partial T}\right)_v = s_0 + \int_{T_0}^{T} dT\, \frac{c_v}{T} + R \ln \frac{v-b}{v_0-b}$$

$$\text{Internal energy}: \quad du = c_v dT + \left[T\left(\tfrac{\partial P}{\partial T}\right)_v - P\right] dv = c_v dT + \tfrac{a}{v^2} dv$$

$$\Rightarrow \quad u = u_0 + \textstyle\int_{T_0}^{T} dT\; c_v - a\left(\frac{1}{v} - \frac{1}{v_0}\right)$$

$$\text{If } c_v = \text{const} \quad \Rightarrow$$

$$s = s_0 + c_v \ln \tfrac{T}{T_0} + R \ln \tfrac{v-b}{v_0-b}, \qquad u = u_0 + c_v (T - T_0) - a\left(\frac{1}{v} - \frac{1}{v_0}\right)$$

“a” is responsible for interaction between molecules => appears in energy

“b” is proportional to volume of molecules => appears in entropy

$$c_P - c_v = T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{1 - \frac{2a(v-b)^2}{RTv^3}} \simeq R\left(1 + \frac{2aP}{R^2T^2}\right)$$

For carbon dioxide at room temperature and P=1 bar the correction is 1%

VDW gas in a reversible adiabatic process

$$s \;=\; s_0 + c_v \ln \tfrac{T}{T_0} + R \ln \tfrac{v-b}{v_0-b} \quad \Rightarrow \quad \text{if } c_v = \text{const}$$

$$s \;=\; \text{const} \quad \Rightarrow \quad c_v \ln T + R \ln(v-b) \;=\; \text{const} \quad \Leftrightarrow \quad T(v-b)^{R/c_v} \;=\; \text{const}$$

VDW gas in a reversible isothermal process

$$\left.\begin{array}{l} \text{The heat absorbed in an isothermal process} \quad \delta Q \;=\; TdS \;=\; RT\,\tfrac{dv}{v-b} \\ \text{The change in internal energy } du \;=\; c_v dT + \tfrac{a}{v^2} dv \quad \Rightarrow \quad du_T \;=\; a\tfrac{dv}{v^2} \end{array}\right\} \Rightarrow$$

$$\Rightarrow \quad \delta w_T \;=\; \delta q_T - \delta u_T \;=\; \left(\frac{RT}{v-b} - \frac{a}{v^2}\right) dv \;=\; P dv$$

$$\Rightarrow \quad \text{the work done in isothermal process} \;\; w \;=\; RT \ln \frac{v_2 - b}{v_1 - b} + a\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$$

Joule and Joule-Thomson experiments

From the 1st law $\quad \eta \equiv \left(\frac{\partial T}{\partial v}\right)_u = -\frac{1}{c_v}\left(\frac{\partial u}{\partial v}\right)_T, \quad \mu \equiv \left(\frac{\partial T}{\partial P}\right)_h = -\frac{1}{c_P}\left(\frac{\partial h}{\partial P}\right)_T.$

1st law + 2nd law $\Rightarrow \quad \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P, \qquad \left(\frac{\partial h}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P + v$

For a van der Waals gas

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2}, \qquad \Rightarrow \qquad \eta = -\frac{a}{c_v v^2}$$

$\Rightarrow$ in Joule experiment $\quad T_2 - T_1 \overset{u=\text{const}}{=} \frac{a}{c_v}\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$

Also, $\quad \left(\frac{\partial h}{\partial P}\right)_T = \frac{RTv^3 b - 2av(v-b)^2}{RTv^3 - 2a(v-b)^2}$

$\Rightarrow$ in Joule – Thomson experiment $\quad \mu = \left(\frac{\partial T}{\partial P}\right)_h = -\frac{1}{c_P}\frac{RTv^3 b - 2av(v-b)^2}{RTv^3 - 2a(v-b)^2}$

$\Rightarrow$ Inversion curve for VDW gas : $\left(\frac{\partial T}{\partial P}\right)_h = 0 \Rightarrow T_{\text{inv}} = \frac{2a(v-b)^2}{Rv^2 b}$

Properties of a liquid or solid under hydrostatic pressure

We assume $\beta = \text{const}$ and $\kappa = \text{const}$

Change of specific volume

$$\begin{aligned} dv &= \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP = \beta v dT - \kappa v dP \\ \Rightarrow v &= v_0 + \int_{T_0}^{T} dT\ \beta v - \int_{P_0}^{P} dP\ \kappa v \end{aligned}$$

For solid or liquid the change of specific volume is small =>

$$\Rightarrow \quad \text{Eqn of state}: \quad v = v_0\left[1 + \beta(T - T_0) - \kappa(P - P_0)\right]$$

The entropy $\quad s = \displaystyle\int_{T_0}^{T} dT\, \frac{c_P}{T} - \int_{P_0}^{P} dP \left(\frac{\partial v}{\partial T}\right)_P + s_0$

$$\left.\begin{aligned} &\text{From the equation of state} \quad \left(\frac{\partial v}{\partial T}\right)_P = \beta v_0, \quad \left(\frac{\partial^2 v}{\partial T^2}\right)_P = 0 \\ &\Rightarrow c_{P_0} = c_P + T\int_{P_0}^{P}\left(\frac{\partial^2 v}{\partial T^2}\right)_P dP \quad \Rightarrow \quad c_P = \text{const} \end{aligned}\right\} \Rightarrow$$

$$\Rightarrow s = c_P \ln\frac{T}{T_0} - \beta v_0 (P - P_0) + s_0$$

Empirical and thermodynamics temperature

$$T \;=\; A\phi(\theta)$$

$\phi(\theta)$ can be determined for a gas near the triple point

Suppose *P* and *U* are known experimentally as functions of *V* and θ

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

T is a function of θ only $\;\Rightarrow\;$ if $T = \text{const}$ then $\theta = \text{const}$ and $\left(\frac{\partial \theta}{\partial T}\right)_V = \frac{d\theta}{dT}$

$$\Rightarrow\; \left(\frac{\partial U}{\partial V}\right)_\theta \;=\; T\left(\frac{\partial P}{\partial \theta}\right)_V \frac{d\theta}{dT} - P \;\Leftrightarrow\; \frac{dT}{T} \;=\; g(\theta)d\theta, \qquad g(\theta) \;\equiv\; \frac{\left(\frac{\partial P}{\partial \theta}\right)_V}{P+\left(\frac{\partial U}{\partial V}\right)_\theta}$$

$$\frac{dT}{T} = g(\theta)d\theta \;\;\Rightarrow\;\; \ln T = \int d\theta\; g(\theta) \;+\; \text{const} \;\;\Rightarrow\;\; T \;=\; Ae^{\int d\theta\;\, g(\theta)}$$

$$\phi(\theta) \;=\; e^{\int d\theta\;\, g(\theta)}$$

$$\text{Example : “Boyle's gas”} \quad PV = f(\theta) \;\;\Rightarrow\;\; \text{we define } \theta \;\equiv\; \theta_3 \frac{PV}{(PV)_3}$$

$$\Rightarrow\;\; P \;=\; \frac{(PV)_3}{\theta_3}\frac{\theta}{V} \;\;\Rightarrow\;\; \left(\frac{\partial P}{\partial \theta}\right)_V \;=\; \frac{(PV)_3}{\theta_3 V}$$

$$\text{From Joule's exp.} \left(\frac{\partial U}{\partial V}\right)_\theta \;=\; 0 \;\;\Rightarrow\;\; g(\theta) \;=\; \frac{(PV)_3}{\theta_3 PV} \;=\; \frac{1}{\theta} \;\;\Rightarrow\;\; T = A\theta$$

Multivariable systems

X - any extensive variable, Y - corresponding intensive variable

$$\delta Q \;=\; dU \;+\; \delta W \;=\; dU \;+\; Y dX$$

$$\frac{\delta Q}{T} \;=\; dS \;=\; \frac{1}{T}dU \;+\; \frac{Y}{T}dX \quad\Rightarrow\quad T(U,X) \;=\; \text{integrating denominator}$$

$$\text{Multivariable systems : extensive } X_1, X_2 \text{ and intensive } Y_1, Y_2$$

$$\text{Example : } \delta W \;=\; P dV - \mathcal{H} dM$$

$$\left.\begin{array}{l} X_1 \text{ and } X_2 - \text{extensive variables (like } V \text{ and } M), \\ Y_1 \text{ and } Y_2 - \text{intensive variables (like } P \text{ and } \mathcal{H}), \end{array}\right\} \Rightarrow$$

$$\delta W \;=\; Y_1 dX_1 + Y_2 dX_2 \Rightarrow \delta Q_r \;=\; dU + \delta W \;=\; dU + Y_1 dX_1 + Y_2 dX_2$$

$$\text{2nd law} \;\Rightarrow\; \frac{Q_2}{Q_1} = \frac{T_2}{T_1} \text{ for Carnot cycle of whatever substance}$$

$$\Rightarrow \quad T \text{ is universal}$$

$$\Rightarrow \quad \frac{\delta Q_r}{T} = dS \;=\; \frac{1}{T}\left(dU + Y_1 dX_1 + Y_2 dX_2\right) \quad - \quad \text{exact differential}$$

$$\Leftrightarrow \quad T(U, X_1, X_2) \;=\; \text{integrating denominator}$$

Caratheodory principle

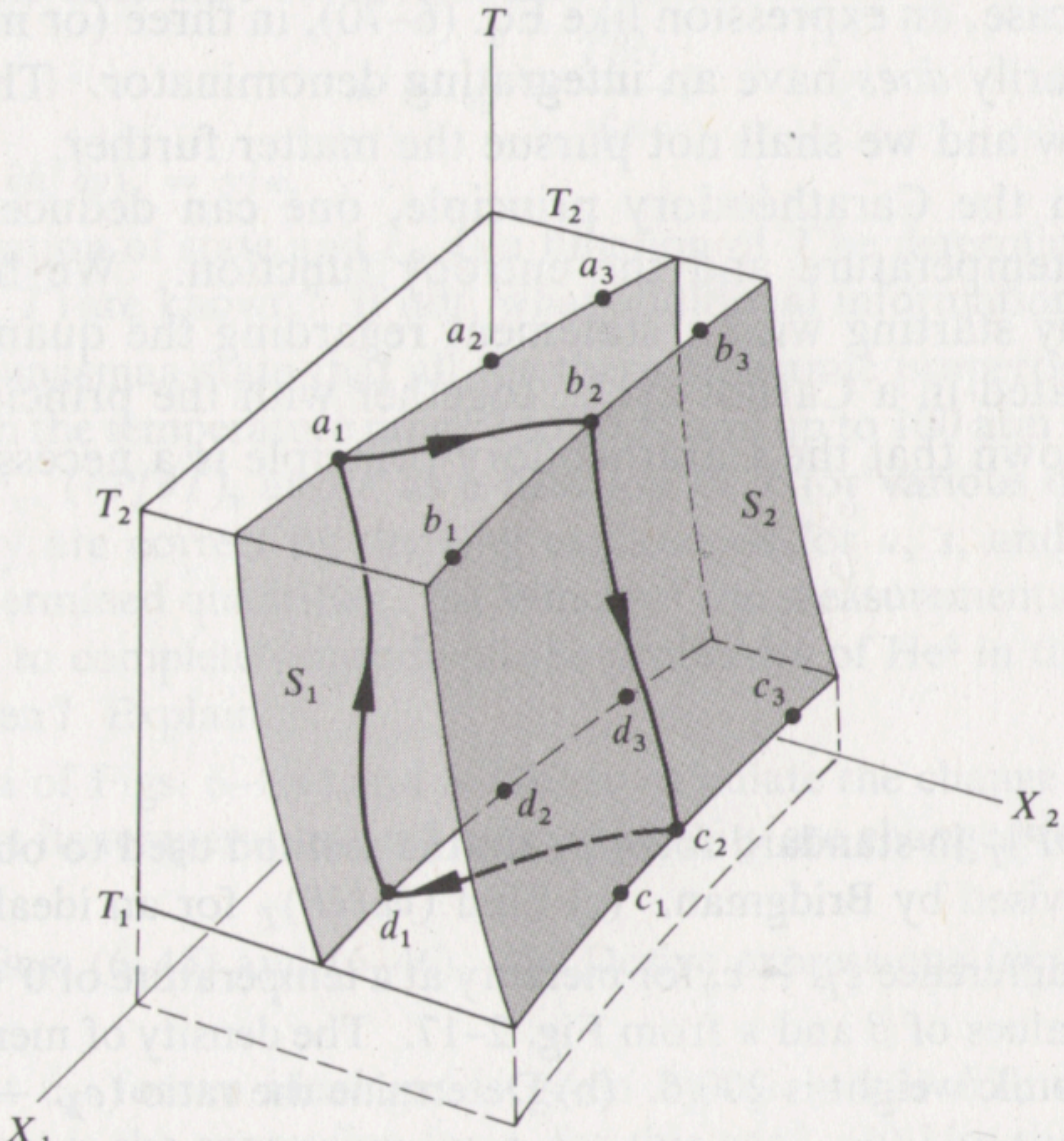


Fig. 6–3 Any process such as a_1-b_2-c_2-d_1-a_1 is a Carnot cycle for a 3-variable system.

$$S = S(T, X_1, X_2)$$

$$S = \text{const is a surface}$$

$$\text{in the } (T, X_1, X_2) \text{ space}$$

Adiabatically accessible states lie either on isentropic surface or in the side of greater entropy

States on the other side are adiabatically inaccessible

Caratheodory's 2nd law:
In the immediate vicinity of every equilibrium state there are states that cannot be reached from the given state by adiabatic process

Thermodynamic potentials

Helmholtz function

For any process between two equilibrium states $W = (U_1 - U_2) + Q$

Let us calculate maximal amount of work that can be obtained when a system undergoes a process between two equilibrium states at a temperature T in the case when the only heat flow is from a single reservoir at the same temperature T

From the 2nd law $\left.\begin{array}{rcl} (S_2 - S_1) + \Delta S_R & \geq & 0 \\ \Delta S_R & = & -\frac{Q}{T} \end{array}\right\} \Rightarrow \quad T(S_1 - S_2) \geq Q$

$\Rightarrow$ from the 1st law $W_T \leq (U_1 - U_2) - T(S_1 - S_2) \equiv F_1 - F_2$

Helmholtz function : $F \equiv U - TS$

$$W_T \;\leq\; F_1 - F_2 \qquad (= \;\text{for a reversible process})$$

Decrease in F sets an upper limit to the work in any process between two equilibrium states at the same temperature. The process can be change of state, change of phase, chemical reaction etc.

$$\text{Assume}\;\; \delta W \;=\; PdV + YdX \;\equiv\; \delta W'_T + \delta A_T$$

$$(\text{for example,}\;\; \delta A_T \equiv YdX \;\;\text{can be}\; HdM)$$

$$\Rightarrow\;\; W'_T + A_T \;\leq\; F_1 - F_2$$

$$\text{In the isochoric process}\quad W'_T = 0 \;\;\Rightarrow\;\; A_T \;\leq\; F_1 - F_2$$

=> The decrease in Helmholtz function sets an upper limit for ``non-PdV” work in a process at constant V and T.

If the process at constant volume is such that A=0 and T=const, Helmholtz function can only decrease or remain the same. Conversely, such process is possible only if $F_2 \;\leq\; F_1$

Gibbs function

Let us define Gibbs function by the equation

$$G \equiv F + PV = H - TS = U - TS + PV$$

=> For two states with same T and P

$$G_1 - G_2 = U_1 - U_2 - T(S_1 - S_2) + P(V_1 - V_2) =$$

$$= F_1 - F_2 + P(V_1 - V_2) \geq W_T + P(V_1 - V_2) = A_T$$

$$\Rightarrow A_T \leq G_1 - G_2$$

=> The decrease in Gibbs function sets an upper limit for ``non-PdV" work in a process at constant V and P.

If the extensive variable X is constant in a process, the only work is ``PdV" work, then A=0 and $G_2 \leq G_1$

In such process Gibbs function either remains constant or decreases

g for an ideal gas

$$\left.\begin{array}{rcl} g &=& h - Ts \;=\; \int_{T_0}^{T} c_P dT - T\int_{T_0}^{T} c_P \frac{dT}{T} + RT\ln\frac{P}{P_0} + h_0 - s_0 T \\ && \qquad\qquad\qquad\qquad\qquad\qquad c_P \;=\; \text{const} \end{array}\right\} \Rightarrow$$

$$g \;=\; h - Ts \;=\; c_P(T - T_0) - c_P T\ln\frac{T}{T_0} + RT\ln\frac{P}{P_0} - s_0(T - T_0) + g_0$$

this can be rewritten as

$$g \;=\; RT[\ln P + \phi(T)]$$

$$RT\phi(T) \;=\; c_P(T - T_0) - c_P T\ln\frac{T}{T_0} - RT\ln P_0 - s_0(T - T_0) + g_0$$

f for an ideal gas

$$\left.\begin{array}{rcl} f &=& u - Ts \;=\; \int_{T_0}^{T} c_v dT - T\int_{T_0}^{T} c_v \frac{dT}{T} + RT\ln\frac{v}{v_0} + u_0 - s_0 T \\ && \qquad\qquad\qquad\qquad\qquad\qquad c_v \;=\; \text{const} \end{array}\right\} \Rightarrow$$

$$f \;=\; u - Ts \;=\; c_v(T - T_0) - c_v T\ln\frac{T}{T_0} - RT\ln\frac{v}{v_0} - s_0(T - T_0) + f_0$$

For the VdW gas

$$f \;=\; c_v(T - T_0) - c_v T\ln\frac{T}{T_0} - a\left(\frac{1}{v} - \frac{1}{v_0}\right) - RT\ln\frac{v - b}{v_0 - b} - s_0(T - T_0) + f_0$$

Thermodynamic potentials

For a *closed* PVT system

$$\left.\begin{array}{lcl} dF &=& dU - TdS - SdT \\ dG &=& dU - TdS - SdT + PdV + VdP \end{array}\right\} \Rightarrow \left\{\begin{array}{lcl} dU &=& TdS - PdV \\ dF &=& -SdT - PdV \\ dG &=& -SdT + VdP \\ dH &=& TdS + VdP \end{array}\right.$$

$$\text{For example, if} \quad U = U(S,V) \quad \Rightarrow \quad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\Rightarrow \quad \left(\frac{\partial U}{\partial S}\right)_V = T, \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\overset{\text{similarly}}{\Rightarrow} \quad \begin{array}{llll} \left(\frac{\partial U}{\partial S}\right)_V = T, & & \left(\frac{\partial U}{\partial V}\right)_S = -P \\ \left(\frac{\partial F}{\partial T}\right)_V = -S & & \left(\frac{\partial F}{\partial V}\right)_T = -P \\ \left(\frac{\partial G}{\partial T}\right)_P = -S, & & \left(\frac{\partial G}{\partial P}\right)_T = V \\ \left(\frac{\partial H}{\partial S}\right)_P = T, & & \left(\frac{\partial H}{\partial P}\right)_S = V \end{array}$$

Gibbs-Helmholtz equations

Suppose that F is known as a function of T and V

$$\left(\frac{\partial F}{\partial T}\right)_V = -S, \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

$$\Rightarrow \begin{cases} P = -\left(\frac{\partial F}{\partial V}\right)_T & \leftarrow \text{ Equation of state,} \\ S = -\left(\frac{\partial F}{\partial T}\right)_V, & \\ U = F + TS = F - T\left(\frac{\partial F}{\partial V}\right)_T & \leftarrow \text{ Energy equation,} \end{cases}$$

Similarly, if G is known as a function of T and P

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V \quad \Rightarrow \quad \begin{cases} V = -\left(\frac{\partial G}{\partial P}\right)_T, \\ S = -\left(\frac{\partial G}{\partial T}\right)_P \\ H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_P \end{cases}$$

Gibbs-Helmholtz equations for multivariable closed systems

Consider system characterised by T plus extensive X_1, X_2 and intensive Y_1, Y_2

System has two equations of state $\Rightarrow$ we can choose any of (T, X_1, X_2), (T, Y_1, Y_2), or (T, X_1, Y_2) to describe the equlibrium state of system.

Let us choose (T, X_1, X_2), then

$$\left.\begin{array}{l} F = U - TS, \quad dF = dU - TdS - SdT \\ dU = TdS - Y_1 dX_1 - Y_2 dX_2 \end{array}\right\} \Rightarrow \quad dF = -SdT - Y_1 dX_1 - Y_2 dX_2$$

$$\Rightarrow \quad \left(\frac{\partial F}{\partial T}\right)_{X_1, X_2} = -S, \qquad \left(\frac{\partial F}{\partial X_1}\right)_{T, X_2} = -Y_1, \qquad \left(\frac{\partial F}{\partial X_2}\right)_{T, X_1} = -Y_2.$$

Let us now choose (T, Y_1, Y_2), then

$$\left.\begin{array}{l} \text{Gibbs function } G \overset{\text{def}}{=} U - TS + Y_1 X_1 + Y_2 X_2 \\ dU = TdS - Y_1 dX_1 - Y_2 dX_2 \end{array}\right\} \Rightarrow \quad dG = -SdT + X_1 dY_1 + X_2 dY_2$$

$$\Rightarrow \quad \left(\frac{\partial G}{\partial T}\right)_{Y_1, Y_2} = -S, \qquad \left(\frac{\partial G}{\partial Y_1}\right)_{T, Y_2} = X_1, \qquad \left(\frac{\partial G}{\partial Y_2}\right)_{T, X_1} = X_2.$$

Let Y_2 be the intensity of a conservative force field,
then the corresponding potential energy $E_p = Y_2 X_2$
and the total energy is $E = U + E_p = U + Y_2 X_2$

$$\text{Define} \quad F^* \overset{\text{def}}{=} E - TS = U - TS + Y_2 X_2$$

The function F^* can be considered a generalized Helmholtz function,
corresponding to $F = U - TS$ for a system whose total energy equals its internal energy only

$$dF^* = dU - TdS - SdT + Y_2 dX_2 \quad \Rightarrow \quad \left(\frac{\partial F^*}{\partial Y_2}\right)_{T,X_1} = X_2$$

Proof

If T, X_1 and X_2 are independent variables,

$$dU = TdS - Y_1 dX_1 - Y_2 dX_2 \quad \Rightarrow \quad \tfrac{\partial}{\partial X_2}\left[U(T,X_1,X_2) - TS(T,X_1,X_2)\right] = -Y_2$$

If T, X_1 and Y_2 are independent variables, $X_2 = X_2(T, X_1, Y_2) \Rightarrow$

$$\begin{aligned}
\left(\tfrac{\partial F^*}{\partial Y_2}\right)_{T,X_1} &\equiv \tfrac{d}{dY_2}\Big(U\left[T,X_1,X_2(T,X_1,Y_2)\right] - TS\left[T,X_1,X_2(T,X_1,Y_2)\right] + Y_2 X_2(T,X_1,Y_2)\Big) \\
&\overset{\text{chain rule}}{=} \tfrac{\partial}{\partial X_2}\Big(U[T,X_1,X_2] - TS[T,X_1,X_2]\Big)\tfrac{\partial X_2(T,X_1,Y_2)}{\partial Y_2} \\
&\qquad + X_2(T,X_1,Y_2) + Y_2 \tfrac{\partial X_2(T,X_1,Y_2)}{\partial Y_2} \\
&= -Y_2 \tfrac{\partial X_2(T,X_1,Y_2)}{\partial Y_2} + X_2(T,X_1,Y_2) + Y_2 \tfrac{\partial X_2(T,X_1,Y_2)}{\partial Y_2} = X_2
\end{aligned}$$

If $T, X_1,$ and Y_2 are independent variables $\quad \left(\frac{\partial F^*}{\partial T}\right)_{X_1,Y_2} = -S$

Proof

$$dU = TdS - Y_1 dX_1 - Y_2 dX_2 \Rightarrow \frac{\partial U(T, X_1, X_2)}{\partial T} = T\frac{\partial S(T, X_1, X_2)}{\partial T}$$

$$dU = TdS - Y_1 dX_1 - Y_2 dX_2 \Rightarrow \frac{\partial U(T, X_1, X_2)}{\partial T} = T\frac{\partial S(T, X_1, X_2)}{\partial T}$$

$$\begin{aligned}
\left(\frac{\partial F^*}{\partial T}\right)_{X_1,Y_2} &\equiv \frac{\partial}{\partial T}\Big(U\left[T, X_1, X_2(T, X_1, Y_2)\right] - TS\left[T, X_1, X_2(T, X_1, Y_2)\right] \\
&\qquad + Y_2 X_2(T, X_1, Y_2)\Big) \\
&= \frac{\partial U[T,X_1,X_2]}{\partial T} - S[T, X_1, X_2] - T\frac{\partial S[T,X_1,X_2]}{\partial T} \\
&\quad + \frac{\partial}{\partial X_2}\Big(U\left[T, X_1, X_2\right] - TS\left[T, X_1, X_2\right]\Big)\frac{\partial X_2(T,X_1,Y_2)}{\partial T} + Y_2\frac{\partial X_2(T,X_1,Y_2)}{\partial T} \\
&= -S[T, X_1, X_2] - Y_2\frac{\partial X_2(T,X_1,Y_2)}{\partial Y_2} + Y_2\frac{\partial X_2(T,X_1,Y_2)}{\partial Y_2} = -S
\end{aligned}$$

Similarly, $\quad \left(\frac{\partial F^*}{\partial X_1}\right)_{T,Y_2} = -Y_1$

Generalized Gibbs-Helmholtz equation

$$dF = -SdT - Y_1dX_1 - Y_2dX_2 \quad \Rightarrow \quad \left(\frac{\partial F}{\partial T}\right)_{X_1,X_2} = -S$$

$$\Rightarrow \quad U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_{X_1,X_2}$$

The enthalpy is defined as $H = U + Y_1X_1 + Y_2X_2$

$$dG = -SdT + X_1dY_1 + X_2dY_2 \quad \Rightarrow \quad \left(\frac{\partial G}{\partial T}\right)_{Y_1,Y_2} = -S$$

$$H = U + Y_1X_1 + Y_2X_2 = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_{Y_1,Y_2}$$

Maxwell relations

$$dz = M(x,y)dx + N(x,y)dy \quad \Rightarrow \quad \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z(x,y)}{\partial x \partial y}$$

$$\Rightarrow \quad \left\{ \begin{array}{llll} \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, & & \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P & & \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \end{array} \right.$$

Stable and unstable equilibrium

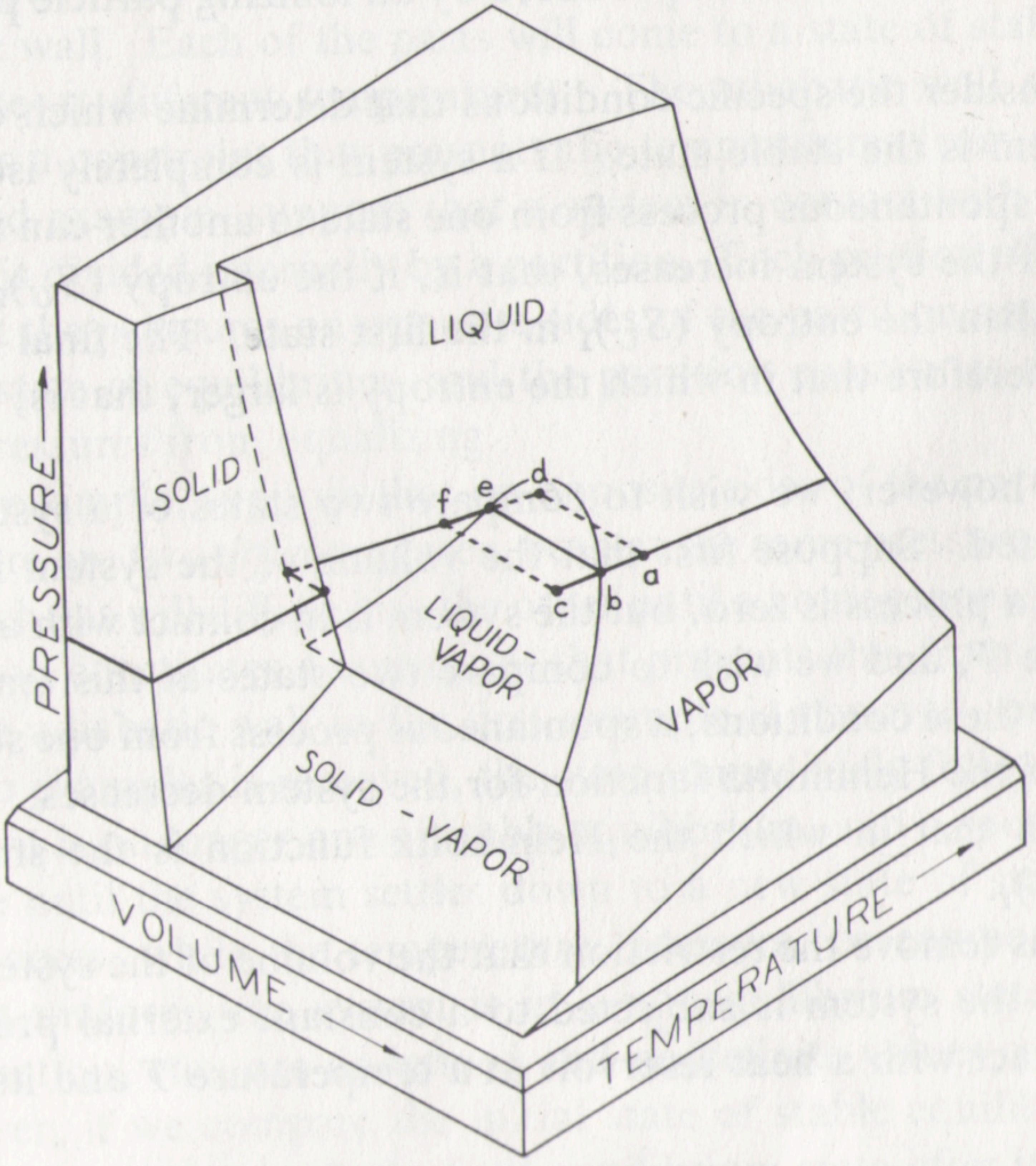


Fig. 7–1 The *P-V-T* surface representing states of stable equilibrium for a pure substance.

``c”: above PVT surface
supercooled vapor
(metastable state)
Use: Wilson chamber

``d”: below PVT surface
superheated liquid
(metastable state)
Use: bubble chamber

We can define entropy ***S***, Helmholtz function ***F*** and Gibbs function ***H*** for the metastable state pretending that it is stable

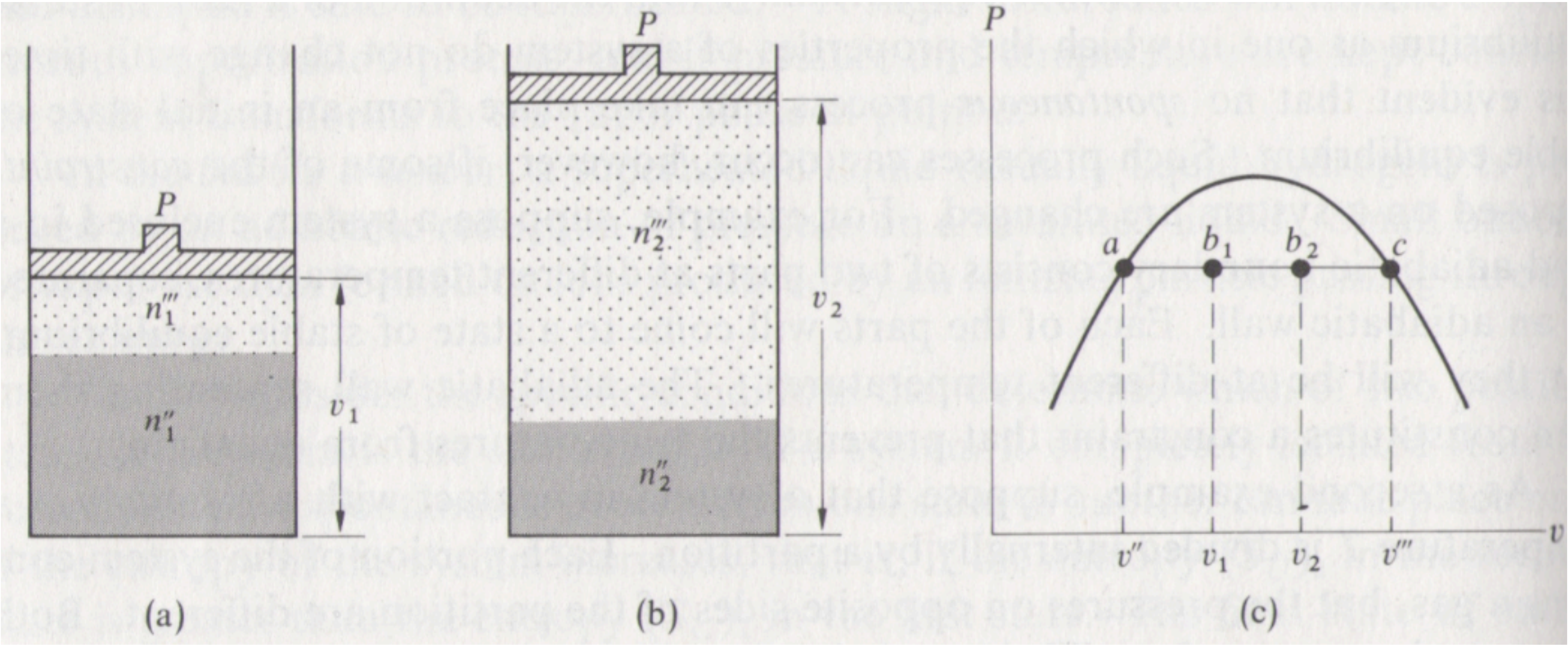
For the isolated system the final state of stable equilibrium is that in which entropy ***S*** is higher

For the system at constant volume and in contact with heat reservoir the final state of stable equilibrium is that in which Helmholtz ***F*** is smaller

For the system at constant pressure and in contact with heat reservoir the final state of stable equilibrium is that in which Gibbs ***G*** is smaller

From the definition of a state of stable equilibrium it is evident that no ***spontaneous*** process can take place from an initial state of stable equilibrium. However, such processes can occur if some of the constraints imposed on a system are changed

Phase transitions



$$\left.\begin{array}{rcl} G_1 &=& n_1''g'' + n_1'''g''', \\ G_2 &=& n_2''g'' + n_2'''g''', \\ n_1'' + n_1''' &=& n_2'' + n_2''', \\ \multicolumn{3}{l}{\text{both states are stable at const } P} \\ \Rightarrow \quad G_1 &=& G_2 \end{array}\right\} \quad \Rightarrow \quad \begin{array}{l} g'' = g''' \\ \text{The specific Gibbs function} \\ \text{has the same value in both phases} \end{array}$$

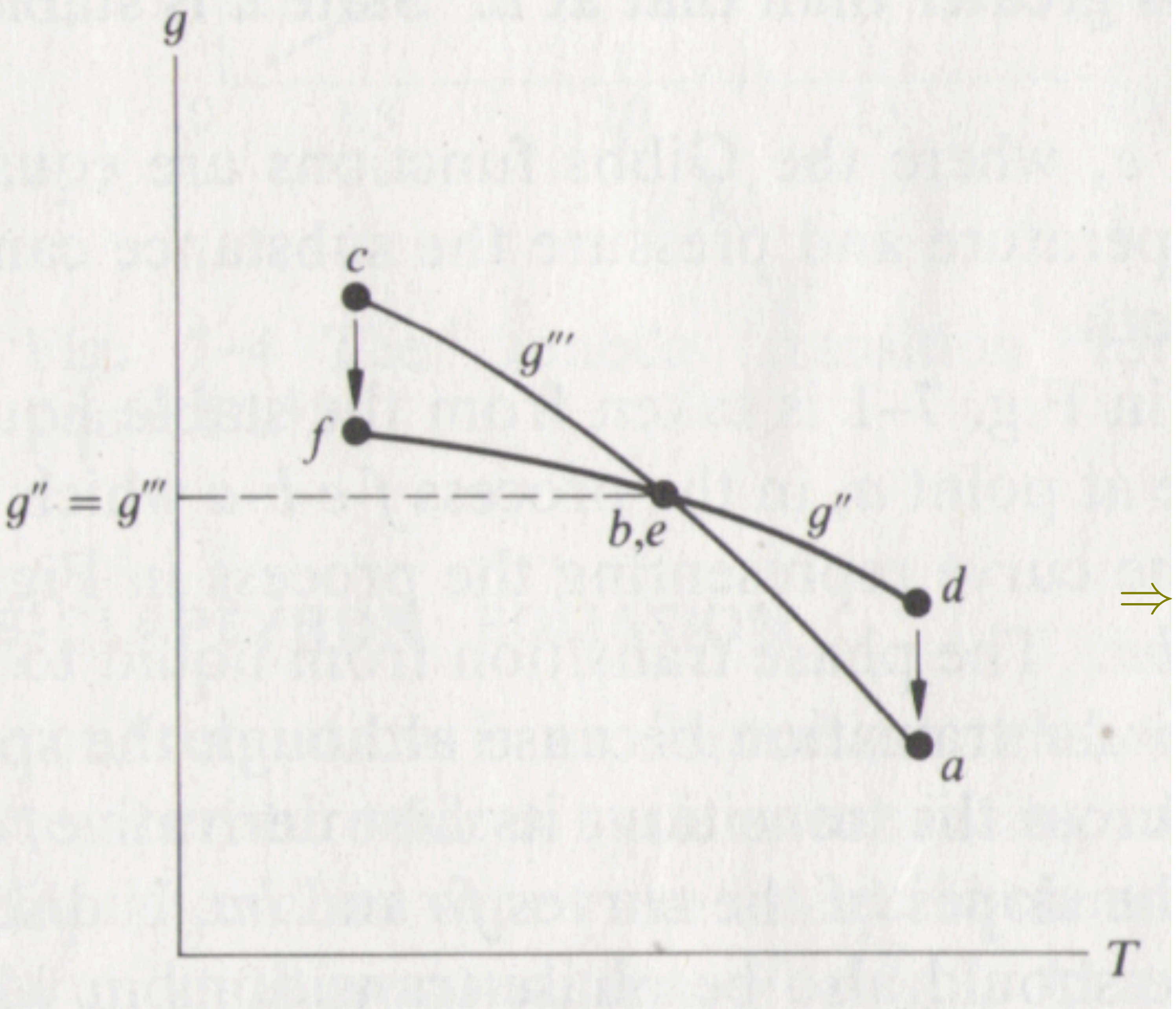


Fig. 7–3 The specific Gibbs function of the vapor and liquid in processes *a-b-c* and *d-e-f* of Fig. 7–1.

$a \to b \to c$ and $d \to e \to f$: processes at constant pressure

$$\left.\begin{aligned} \left(\frac{\partial g''}{\partial T}\right)_P &= -s'' \\ \left(\frac{\partial g'''}{\partial T}\right)_P &= -s''' \\ s''' - s'' &= \frac{l_{23}}{T} \end{aligned}\right\}$$

$$\Rightarrow \quad \left(\frac{\partial g''}{\partial T}\right)_P - \left(\frac{\partial g'''}{\partial T}\right)_P = \frac{l_{23}}{T} > 0$$

c - metastable

f - stable

d - metastable

a - stable

$b \to e$: first – order phase transition $\Leftarrow$ g is continuous but $\left(\frac{\partial g}{\partial T}\right)_P$ is not

$\text{Second} - \text{order phase transition :}$

g and $\left(\frac{\partial g}{\partial T}\right)_P$ are continuous but $\left(\frac{\partial^2 g}{\partial T^2}\right)_P$ is not

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_P = -\left(\frac{\partial s}{\partial T}\right)_P = -\frac{c_P}{T} \quad \Rightarrow$$

the value of c_P must be different in two phases

Example: transition of a superconductor from superconducting to normal state at zero magnetic field

λ – transition in liquid helium

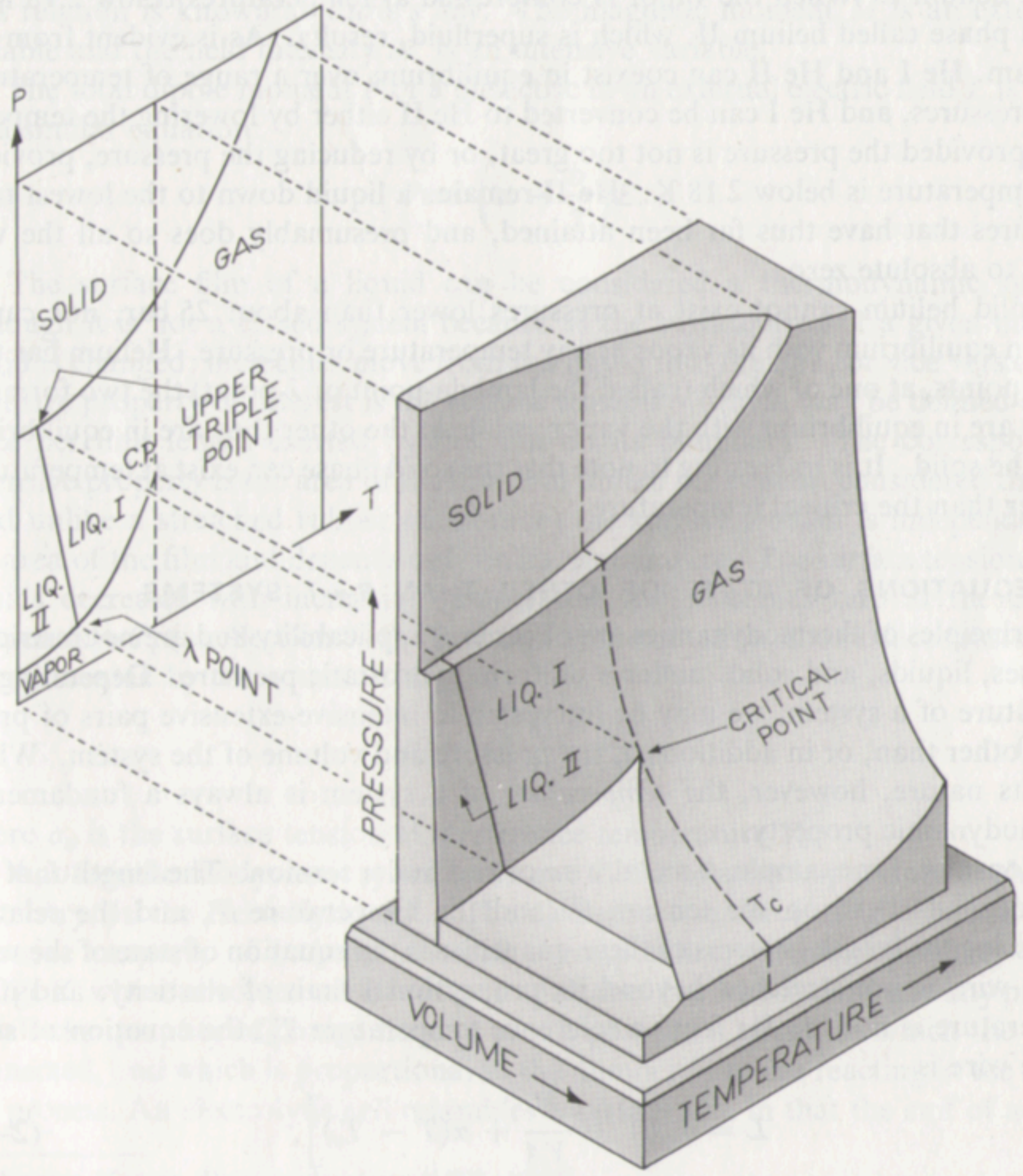


Fig. 2–13 *P-v-T* surface for helium with projection onto the *P-T* plane.

c_P *versus* T

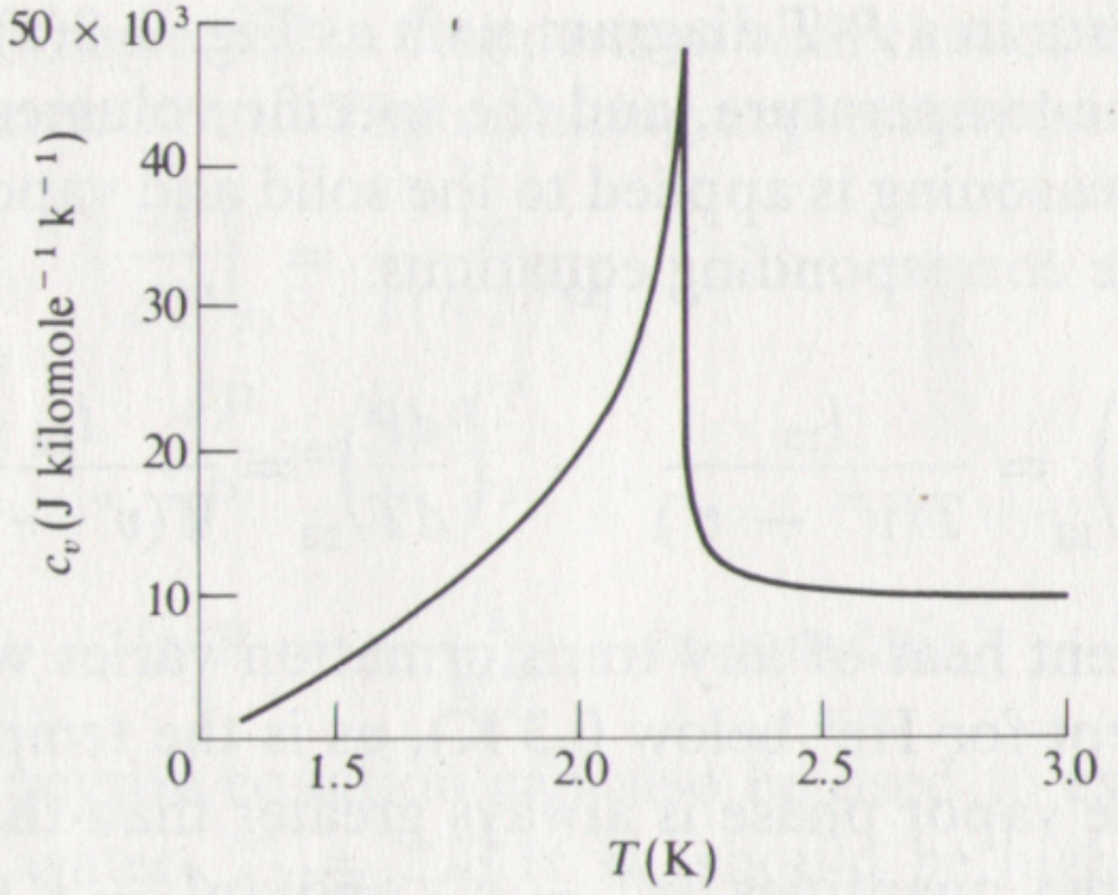


Fig. 7–4 The lambda transition for liquid He^4.

Liq. I - ordinary liquid
Liq. II -superfluid liquid

Clausius-Clapeyron equation

If liquid and vapor are at equilibrium at pressure P and temperature T   g”=g”’.
At a temperature T+dT and pressure P+dP   g”+dg” = g”’+dg”’ => dg”=dg”’

$$\left.\begin{aligned} dg &= -sdT + vdP \;\Rightarrow \\ -s''dT + v''dP &= -s'''dT + v'''dP \\ \Rightarrow\; (s''' - s'')dT &= (v''' - v'')dP, \\ s''' - s'' &= \frac{l_{23}}{T} \end{aligned}\right\} \Rightarrow$$

$$\left(\frac{\partial P}{\partial T}\right)_{2\to 3} = \frac{l_{23}}{T(v''' - v'')}$$

$$\text{Clausius} - \text{Clapeyron equation for liquid} - \text{vapor equilibrium}$$

$$\text{for solid} - \text{vapor transition} \qquad \left(\frac{\partial P}{\partial T}\right)_{1\to 3} = \frac{l_{13}}{T(v''' - v')}$$

$$\text{for solid} - \text{liquid transition} \qquad \left(\frac{\partial P}{\partial T}\right)_{1\to 2} = \frac{l_{13}}{T(v'' - v')}$$

The third law of thermodynamics

In a spontaneous process (like chemical reaction) at a constant pressure and in contact with reservoir at temperature T the G-H equation gives

$$G_2 - G_1 \;=\; H_2 - H_1 + T\Big(\frac{\partial[G_2 - G_1]}{\partial T}\Big)_P \;\Leftrightarrow\; \Delta G \;=\; \Delta H + T\Big(\frac{\partial \Delta G}{\partial T}\Big)_P$$

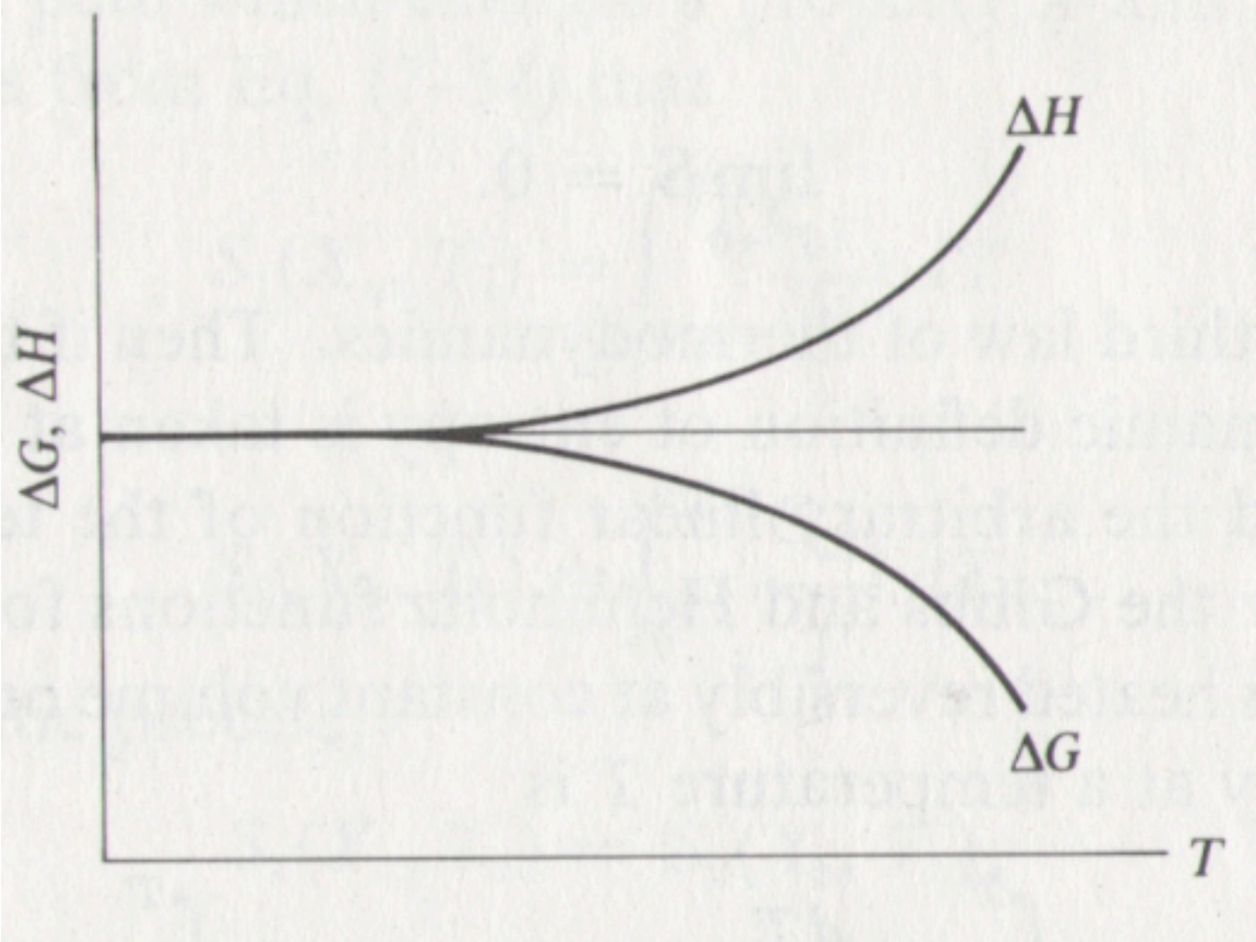


Fig. 7–5 The temperature dependence of the change in the Gibbs function and in the enthalpy for an isobaric process.

From experiments

$$\begin{aligned} \lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right)_P &= 0, \\ \lim_{T\to 0}\left(\frac{\partial \Delta H}{\partial T}\right)_P &= 0 \end{aligned}$$

$$\begin{aligned} \lim_{T\to 0}\left(\frac{\partial [G_2 - G_1]}{\partial T}\right)_P &= 0 \\ = \lim_{T\to 0}\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right], \end{aligned}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\Rightarrow \lim_{T\to 0}(S_1 - S_2) = 0$$

Nernst heat theorem:

In the neighborhood of absolute zero, all reactions a liquid or solid in internal equilibrium take place with no change in entropy.

$$\text{Planck}: \quad \text{the entropy of every solid and liquid substance in internal equilibrium at absolute zero is itself zero}: \quad \lim_{T \to 0} S \;=\; 0$$

$$\left.\begin{array}{l} S(V,T) \;=\; \int_0^T C_V \frac{dT}{T}, \quad S(V,T) \;=\; \int_0^T C_P \frac{dT}{T} \\ \text{entropy is finite} \end{array}\right\} \;\Rightarrow\; \lim_{T \to 0} C_V \;=\; \lim_{T \to 0} C_P \;=\; 0$$

It is impossible to reduce the temperature of a system to absolute zero in any finite number of operations

Proof: consider reversible adiabatic process which changes temperature T and some other property X of the system

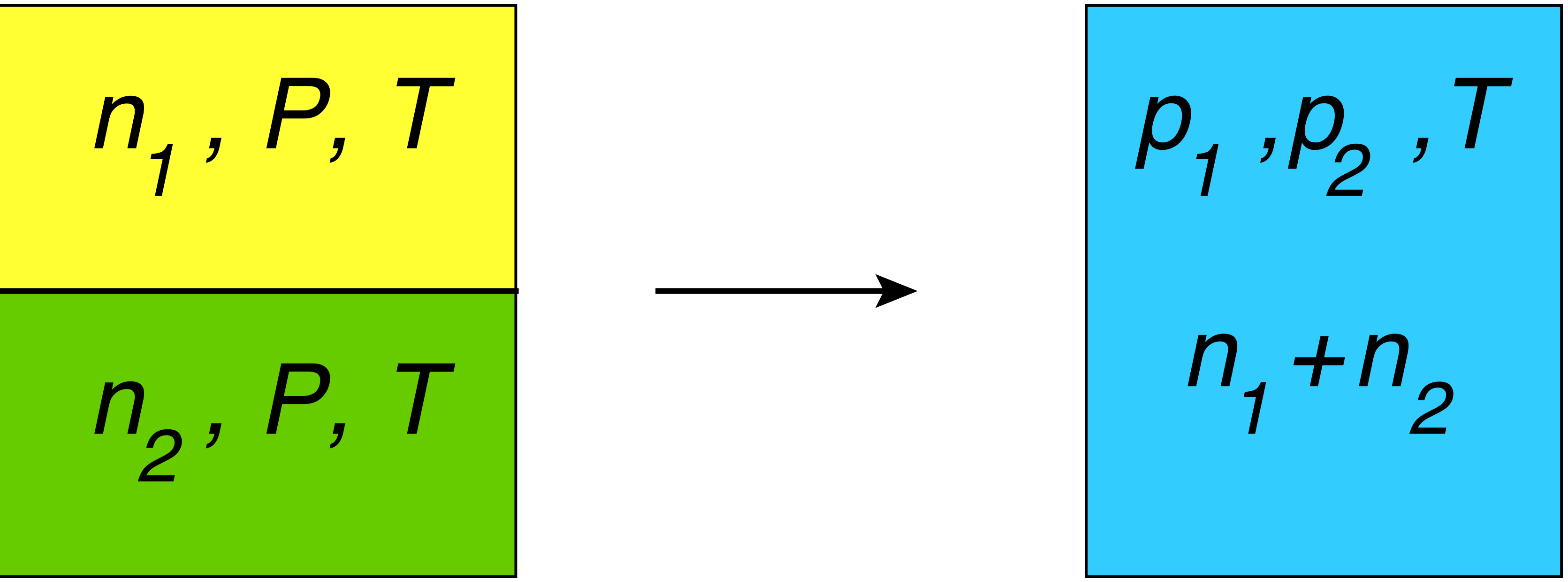
$$\left.\begin{array}{l} S_1(X_a,T_a) \;=\; \int_0^{T_a} dT \frac{C_X}{T}, \quad S_1(X_b,T_b) \;=\; \int_0^{T_b} dT \frac{C_X}{T} \\ \\ \text{adiabatic process} \;\Rightarrow\; S_1 = S_2 \;\Rightarrow\; \int_0^{T_a} dT \frac{C_X}{T} \;=\; \int_0^{T_b} dT \frac{C_X}{T} \end{array}\right\} \;\Rightarrow$$

$$\text{take } T_b \to 0 \;\Rightarrow\; \int_0^{T_a} dT \frac{C_X}{T} \;=\; 0 \qquad \leftarrow \quad \text{contradiction}$$

Applications of Thermodynamics

Chemical potential

Diffusion of two ideal gases at same T and P:



n_1, P, T

n_2, P, T

p_1, p_2, T

$n_1 + n_2$

Experiment:

$p_1 + p_2 = P$

$$\text{Gibbs function for an ideal gas}: \quad g = RT[\ln P + \phi(T)],$$

$$\phi(T) = \frac{c_P - s_0}{R}\left(1 - \frac{T_0}{T}\right) - \frac{c_P}{R}\ln\frac{T}{T_0} - \ln P_0 + \frac{g_0}{RT}$$

$$\text{Initial Gibbs function}: \quad G_i = n_1 g_{1i} + n_2 g_{2i}$$

$$g_{1i} = RT(\ln P + \phi_1), \quad g_{2i} = RT(\ln P + \phi_2),$$

Final Gibbs function $G_i = n_1 g_{1i} + n_2 g_{2i}$

$$g_{1i} = RT(\ln p_1 + \phi_1), \quad g_{2i} = RT(\ln p_2 + \phi_2),$$

Mole fractions : $x_1 = \frac{n_1}{n_1+n_2}, \quad x_2 = \frac{n_2}{n_1+n_2}, \quad n \equiv n_1 + n_2$

$$n_1 = \frac{p_1 V}{RT}, \quad n_2 = \frac{p_2 V}{RT}, \quad n = \frac{PV}{RT} \quad \Rightarrow \quad x_1 = \frac{p_1}{P}, \; x_2 = \frac{p_2}{P}$$

$$\ln p_1 = \ln P + \ln x_1, \quad \ln p_2 = \ln P + \ln x_2 \quad \Rightarrow$$

$$g_{1f} = RT(\ln P + \phi_1 + \ln x_1), \quad g_{2f} = RT(\ln P + \phi_2 + \ln x_2)$$

The *chemical potential* of each gas in the mixture is defined as

$$\mu \equiv RT(\ln P + \phi + \ln x) = RT(\ln p + \phi) = g + RT \ln x$$

The change of Gibbs function in the mixing process is

$$G_f - G_i = n_1(\mu_1 - g_1) + n_2(\mu_2 - g_2) = RT(n_1 \ln x_1 + n_2 \ln x_2)$$

Chemical potential for open systems

$$\left.\begin{array}{l} \text{Closed system :} \quad dU \;=\; TdS - PdV, \\ U = U(S,V) \quad \Rightarrow \quad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \end{array}\right\} \Rightarrow \quad \left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Open system: we can add or remove material

$$\left.\begin{array}{l} dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{V,S} dn, \\ dn = 0 \quad \Rightarrow \quad dU \;=\; TdS - PdV, \end{array}\right\} \Rightarrow \quad \left(\frac{\partial U}{\partial S}\right)_{V,n} = T, \quad \left(\frac{\partial U}{\partial V}\right)_{S,n} = -P$$

$$\text{Definition :} \qquad \mu \;\equiv\; \left(\frac{\partial U}{\partial n}\right)_{V,S} \quad - \quad \text{chemical potential}$$

$$\Rightarrow \quad \text{for open system} \qquad dU \;=\; TdS - PdV + \mu dn$$

In general : $dU = TdS - YdX + \mu dn$

$$S = S(U, X, n) \;\Rightarrow\; dS = \frac{1}{T}dU + \frac{Y}{T}dX - \frac{\mu}{T}dn \;\Rightarrow\; \mu = -T\left(\frac{\partial S}{\partial n}\right)_{U,X}$$

$$F = F(U, X, n) \;\Rightarrow\; dF = dU - TdS - SdT = -SdT - YdX + \mu dn \;\Rightarrow\; \mu = \left(\frac{\partial F}{\partial n}\right)_{T,X}$$

$$G(U, Y, n) = F + YX \;\Rightarrow\; dG = -SdT + XdY + \mu dn \;\Rightarrow\; \mu = \left(\frac{\partial G}{\partial n}\right)_{T,Y}$$

Phase equilibrium and phase rule

Consider a phase composed of k constituents

$$U = U(S, V, n_1, n_2, ..., n_k) \Rightarrow$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} + \left(\frac{\partial U}{\partial V}\right)_{S,n} + \left(\frac{\partial U}{\partial n_1}\right)_{V,S,n'} + \left(\frac{\partial U}{\partial n_2}\right)_{V,S,n'} + ... + \left(\frac{\partial U}{\partial n_k}\right)_{V,S,n'}$$

$$\Rightarrow \quad dU = TdS - PdV + \mu_1 dn_1 + ... + \mu_k dn_k \quad \text{where} \quad \mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n'}$$

Similarly, for fixed T and P

$$\left.\begin{aligned} dG &= dU - TdS + PdV \Rightarrow \\ dU &= TdS - PdV + \mu_1 dn_1 + ... + \mu_k dn_k \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} dG &= \mu_1 dn_1 + ... + \mu_k dn_k \\ \Rightarrow \quad \mu_i &= \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n'} \end{aligned}\right.$$

Chemical potentials do not depend on the overall size of the phase.

Proof: gedanken experiment on phase consisting of two equal parts

$$\text{for each half } \mu_i = \frac{\Delta G}{\Delta n_i} \qquad vs \qquad \text{for two halves } \mu_i = \frac{2\Delta G}{2\Delta n_i} = \frac{\Delta G}{\Delta n_i}$$

We get for ***k*** constituents at temperature ***T*** and pressure ***P***

$$\begin{aligned}
G &= \mu_1 n_1 + \mu_2 n_2 + ... + \mu_k n_k + G_0 \\
U &= TS - PV + \mu_1 n_1 + \mu_2 n_2 + ... + \mu_k n_k + G_0 \\
H &= TS + \mu_1 n_1 + \mu_2 n_2 + ... + \mu_k n_k + G_0 \\
F &= -PV + \mu_1 n_1 + \mu_2 n_2 + ... + \mu_k n_k + G_0
\end{aligned}$$

Consider ***k*** constituents in ***r*** phases at temperature ***T*** and pressure ***P***.

(In real life, gas is only one, but liquids and solids can be few)

We had a rule that g is the same for each phase in equilibrium.

For several constituents, this rule should be modified.

$$G = \sum_{j=1}^{r}\sum_{i=1}^{k}\mu_i^{(j)} n_i^{(j)} \quad \overset{G=G_{\min}}{\Rightarrow} \quad (dG)_{T,P} = \sum_{j=1}^{r}\sum_{i=1}^{k}\mu_i^{(j)} dn_i^{(j)} = 0$$

We get a system of equations

$$\begin{aligned}
0 \quad = \quad & \mu_1^{(1)} dn_1^{(1)} + \mu_1^{(2)} dn_1^{(2)} + \dots + \mu_1^{(r)} dn_1^{(r)} \\
+ \quad & \mu_2^{(1)} dn_2^{(1)} + \mu_2^{(2)} dn_2^{(2)} + \dots + \mu_2^{(r)} dn_2^{(r)} \\
. \\
. \\
+ \quad & \mu_k^{(1)} dn_k^{(1)} + \mu_k^{(2)} dn_k^{(2)} + \dots + \mu_k^{(r)} dn_k^{(r)}
\end{aligned}$$

with constraints

$$\begin{aligned}
dn_1^{(1)} + dn_1^{(2)} + \dots + dn_1^{(r)} &= 0 \\
dn_2^{(1)} + dn_2^{(2)} + \dots + dn_2^{(r)} &= 0 \\
. \\
. \\
dn_k^{(1)} + dn_k^{(2)} + \dots + dn_k^{(r)} &= 0
\end{aligned}$$

To solve this system, consider $n_i^{(j\geq 2)}$ as independent variables and express $dn_i^{(1)}$ as $dn_i^{(1)} = -dn_i^{(2)} - \ldots - dn_i^{(r)}$

=> we get a system

$$\begin{aligned}
0 \quad = \quad & (\mu_1^{(2)} - \mu_1^{(1)})dn_1^{(2)} + (\mu_1^{(3)} - \mu_1^{(1)})dn_1^{(3)} + \ldots + (\mu_1^{(r)} - \mu_1^{(1)})dn_1^{(r)} \\
+ \quad & (\mu_2^{(2)} - \mu_2^{(1)})dn_2^{(2)} + (\mu_2^{(3)} - \mu_2^{(1)})dn_2^{(3)} + \ldots + (\mu_2^{(r)} - \mu_2^{(1)})dn_2^{(r)} \\
. \quad & \\
. \quad & \\
+ \quad & (\mu_k^{(2)} - \mu_k^{(1)})dn_k^{(2)} + (\mu_k^{(3)} - \mu_k^{(1)})dn_k^{(3)} + \ldots + (\mu_k^{(r)} - \mu_k^{(1)})dn_k^{(r)}
\end{aligned}$$

Now $n_i^{(j\geq 2)}$ are independent and can be varied arbitrarily $\Rightarrow$

$\mu_1^{(2)} = \mu_1^{(1)}, \quad \mu_1^{(3} = \mu_1^{(1)}, \ldots, \mu_1^{(r)} = \mu_1^{(1)} \quad \Rightarrow \quad \mu_1^{(1)} = \mu_1^{(2)} = \ldots = \mu_1^{(r)}$

Similarly, $\mu_2^{(1)} = \mu_2^{(2)} = \ldots = \mu_2^{(r)}, \ldots, \mu_k^{(1)} = \mu_k^{(2)} = \ldots = \mu_k^{(r)}$

$\Rightarrow$ the upper index in μ is redundant : $\mu_i^{(j)} \equiv \mu_i$

Gibbs phase rule

$k(r-1)$ equations of phase equilibrium :
$$\begin{cases} \mu_1^{(1)} = \mu_1^{(2)} = \ldots = \mu_1^{(r)} \\ \mu_2^{(1)} = \mu_2^{(2)} = \ldots = \mu_2^{(r)} \\ . \\ . \\ \mu_k^{(1)} = \mu_k^{(2)} = \ldots = \mu_k^{(r)} \end{cases}$$

$r(k-1)+2$ unknowns $\quad (r(k-1)$ for r mole fractions and 2 for T and $P)$

$r(k-1)+2 = k(r-1) \quad \Rightarrow \quad$ *nonvariant* system with *zero variance*,
$r(k-1)+2 = k(r-1)+1 \quad \Rightarrow \quad$ *monovariant* system with variance 1,
$r(k-1)+2 = k(r-1)+f \quad \Rightarrow \quad$ system with variance f,

Gibbs phase rule : $\quad f = k - r + 2 \quad$ (no chemical reactions)

Example: water in equilibrium with vapor

$k = 1$ and $r = 2 \quad \Rightarrow \quad f = k - r + 2 = 1 \quad \Rightarrow \quad T$ or P can be $\forall$

Another example: triple point of ice, water, and vapor

$$f \;=\; k - r + 2 \;=\; 0 \quad\Rightarrow\quad T \text{ and } P \text{ are fixed}$$

Variance in systems with chemical reactions

Example: four constituents A, B, C, and D.

$$n_A A + n_B B \quad \overset{\text{chemical reaction}}{\longleftrightarrow} \quad n_C C + n_D D$$

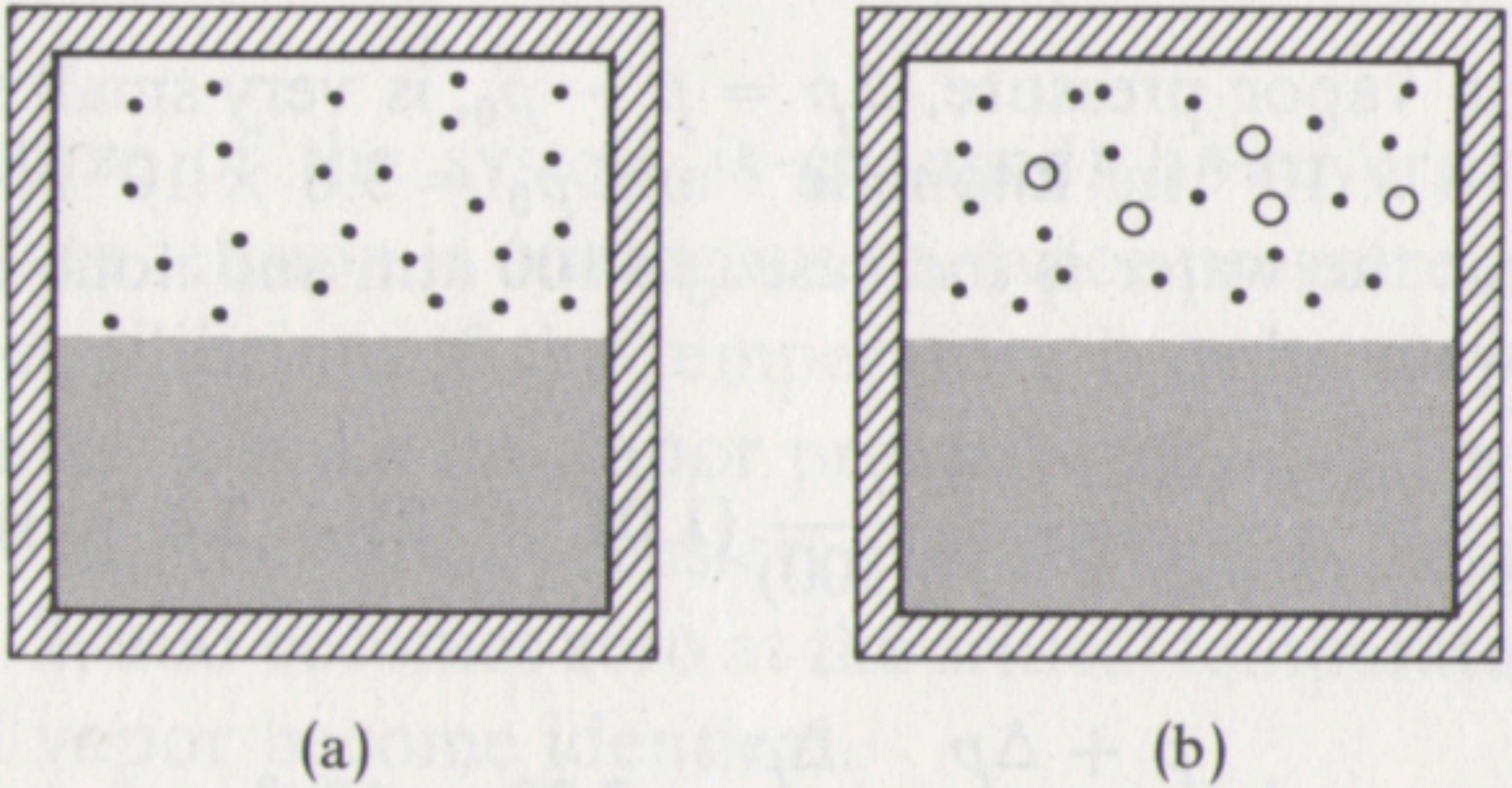
Number of variables is the same but there is one more equation

$$\Rightarrow \quad f \;=\; r(k-1) + 2 - [k(r-1)+1] \;=\; k - r + 1$$

In general $f \;=\; k - \eta - r + 2$

$\eta \;\equiv\;$ number of independent reversible chemical reactions

Example: dependence of vapor pressure on total pressure



(a) (b)

Fig. 8–1 A liquid in equilibrium with its vapor (a) at the vapor pressure, (b) at a higher pressure caused by the presence of an indifferent gas.

P :
total pressure

p :
vapor pressure

For liquid

$$\mu'' = \left(\frac{\partial G}{\partial n}\right)_{T,P,n'=0} = g''$$

For vapor

$$\mu''' = RT(\ln p + \phi)$$

Gas pumped in at constant T so that $P \to P + dP$ and $p \to p + dp$

The system is at equilibrium at new P $\Rightarrow$ $d\mu'' = d\mu'''$

$$\left.\begin{array}{l} \text{Temperature is constant } \Rightarrow \\ \text{For the liquid } d\mu'' = dg'' = -s''dT + v''dP = v''dP \\ \text{For the vapor } \phi = \phi(T) \Rightarrow d\mu''' = \frac{RT}{p}dp \end{array}\right\} \Rightarrow$$

$$\Rightarrow \left\{\begin{array}{lcl} \mu'' & = & \mu''' \Rightarrow \\ v''dP & = & RT\frac{dp}{p} \end{array}\right. \Rightarrow \frac{dp}{p} = \frac{v''}{RT}dP$$

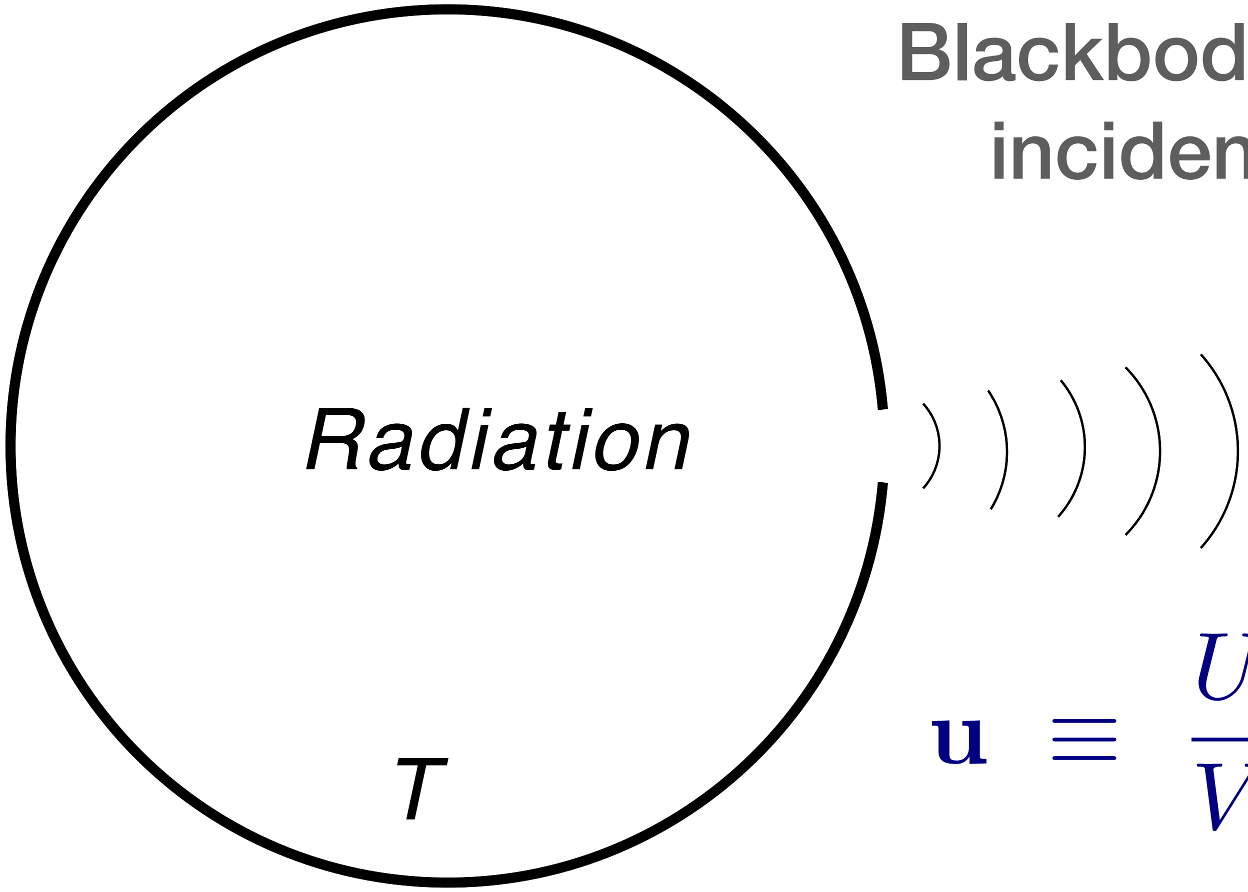
If no indifferent gas is present $P = p_0 \Rightarrow$

$$v''dP = RT\frac{dp}{p} \Rightarrow \int_{p_0}^{p}\frac{dp}{p} = \frac{v''}{RT}\int_{p_0}^{P}dP$$

$$\Rightarrow \ln\frac{p}{p_0} = \frac{v''}{RT}(P - p_0)$$

When the total pressure ***P*** is increased, the vapor pressure ***p*** increases also => as more of the indifferent gas is pumped in, more of the liquid evaporates

Blackbody radiation



Blackbody absorbs 100% radiation incident on it at any frequency

$$\mathbf{u} \equiv \frac{U}{V} - \text{radiant energy density}$$

$$\left.\begin{array}{l}\text{Experiment : the rate of radiation is a function of } T \text{ only}\\ \text{Rate of radiation is proportional to } \mathbf{u}\end{array}\right\} \Rightarrow \mathbf{u} = \mathbf{u}(T)$$

From experiment : Planck's law $d\mathbf{u} = \frac{c_1\nu^3}{e^{\frac{c_2\nu}{T}}-1}$ $\nu \equiv$ frequency

$$\Rightarrow \mathbf{u} = \int d\mathbf{u} = \int_0^\infty d\nu \frac{c_1\nu^3}{e^{\frac{c_2\nu}{T}}-1} \sim T^4$$

The dependence of ***u*** on ***T*** can be explained by thermodynamics

From electrodynamics :

the pressure exerted on walls by radiation $P = \frac{\mathbf{u}}{3}$

$$\left.\begin{array}{l} \left(\frac{dU}{dV}\right)_T = T\left(\frac{dP}{dT}\right)_V - P \Rightarrow T\left(\frac{dP}{dT}\right)_V = \mathbf{u} + P \\ P = \frac{\mathbf{u}}{3} \Rightarrow \left(\frac{dP}{dT}\right)_V = \frac{1}{3}\left(\frac{d\mathbf{u}}{dT}\right)_V = \frac{1}{3}\frac{d\mathbf{u}}{dT} \end{array}\right\} \Rightarrow$$

$$\Rightarrow \left\{\begin{array}{l} \mathbf{u} = \frac{T}{3}\frac{d\mathbf{u}}{dT} - \frac{1}{3}\mathbf{u} \\ \Rightarrow \mathbf{u} \sim T^4 \end{array}\right.$$

$$\mathbf{u} = \sigma T^4, \qquad \sigma = 7.561 \times 10^{-16}\frac{\mathrm{J}}{\mathrm{m}^3\mathrm{K}^4}$$

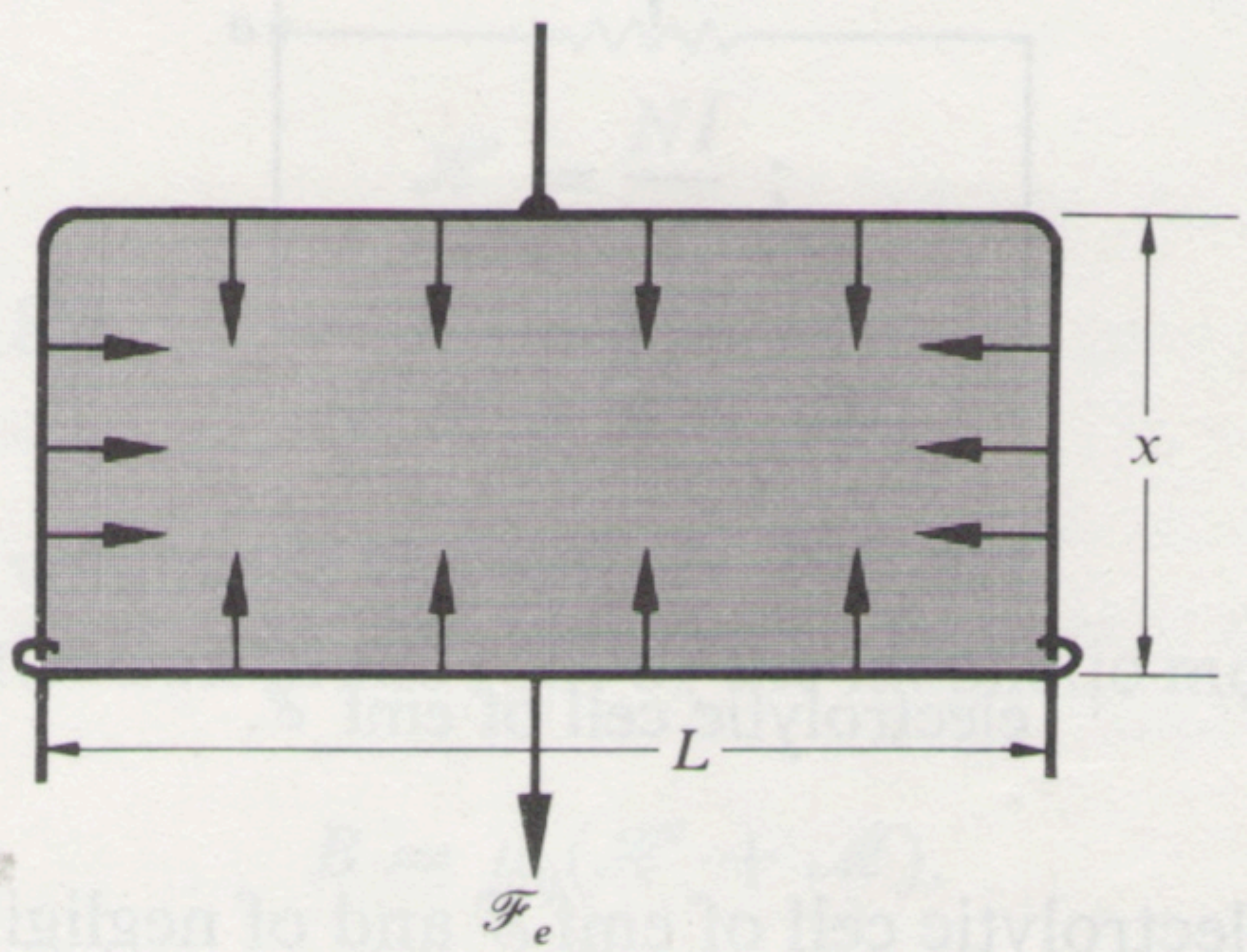
Equation of state $P = \frac{1}{3}\mathbf{u} = \frac{1}{3}\sigma T^4$, energy equation $U = \mathbf{u}V = \sigma V T^4$

$$\left(\frac{\partial U}{\partial T}\right)_V = 4\sigma V T^3 \Rightarrow S = \int_0^T C_V \frac{dT}{T} = \frac{4}{3}\sigma V T^3$$

Helmholtz function $F = U - TS = -\frac{1}{3}\sigma V T^4$

Gibbs function $G = F + PV = -\frac{1}{3}\sigma V T^4 + \frac{1}{3}\sigma V T^4 = 0$

Surface tension



Two ``phases”: surface film and bulk liquid

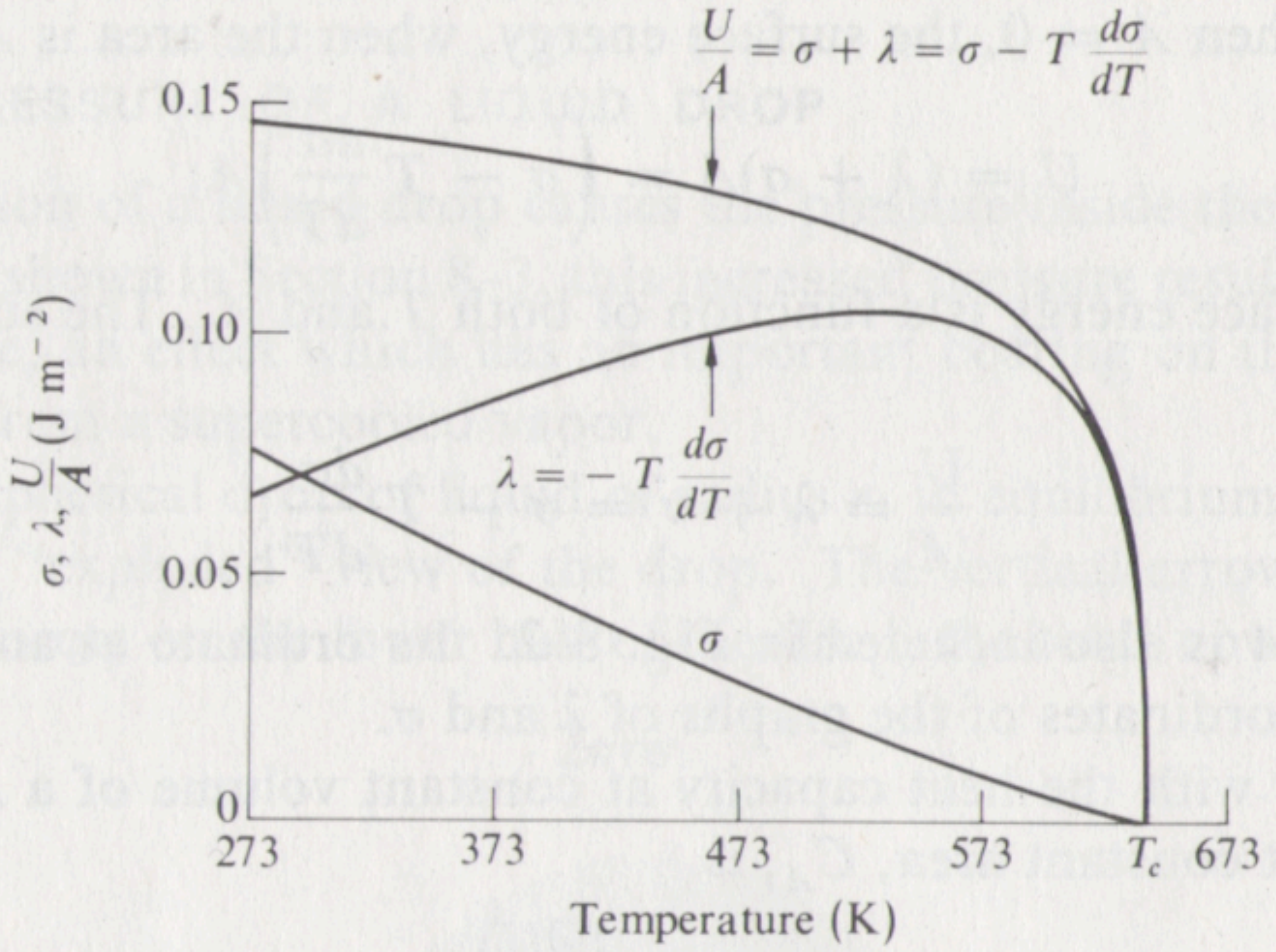


Fig. 8–2 Surface tension σ, “latent heat” λ, and surface energy per unit area U/A, for water, as a function of temperature.

λ = the heat supplied per unit increase of area at constant T

surface tension σ : force per unit length of boundary

Isothermal process : the heat flow into the film $\delta Q_T = \lambda dA_T$
the work is $\delta W = -\sigma dA_T$
and the increase in internal *surface energy* is

$$\delta U_T = \delta Q_T - \delta W_T = (\lambda + \sigma) dA_T \Rightarrow \left(\frac{\partial U}{\partial A}\right)_T = \lambda + \sigma$$

Recall $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$

By analogy $\sigma \sim -P$ and $A \sim V$ we can write

$$\left(\frac{\partial U}{\partial A}\right)_T = \sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_A \overset{\sigma=\sigma(T)}{=} \sigma - T\frac{d\sigma}{dT}$$

$$\left(\frac{\partial U}{\partial A}\right)_T = \lambda + \sigma, \quad \left(\frac{\partial U}{\partial A}\right)_T = \sigma - T\frac{d\sigma}{dT} \Rightarrow \lambda = -T\frac{d\sigma}{dT}$$

$$U = (\lambda + \sigma)A = \left(\sigma - T\frac{d\sigma}{dT}\right)A \Rightarrow \frac{U}{A} = \sigma - T\frac{d\sigma}{dT}$$

By analogy with heat capacity in PVT system, one can define

$$c_A \equiv \left(\frac{\partial U}{\partial T}\right)_A$$

$$U = \left(\sigma - T\frac{d\sigma}{dT}\right)A \Rightarrow C_A = A\left[\frac{d\sigma}{dT} - T\frac{d^2\sigma}{dT^2} - \frac{d\sigma}{dT}\right] = -AT\frac{d^2\sigma}{dT^2}$$

$\Rightarrow$ The specific capacity per unit area is $c_A = -T\dfrac{d^2\sigma}{dT^2}$

Helmholtz function and entropy

By analogy with $U = F - T\left(\frac{dF}{dT}\right)_V$ we can find $U = F - T\left(\frac{dF}{dT}\right)_A$

$U = \left(\sigma - T\frac{d\sigma}{dT}\right)A \Rightarrow F = \sigma A \Rightarrow \sigma = \frac{F}{A}$

The entropy of the film is $S = -\left(\frac{dF}{dT}\right)_A = -A\frac{d\sigma}{dT}$

$\Rightarrow s = -\frac{d\sigma}{dT}$

Vapor pressure of a liquid drop

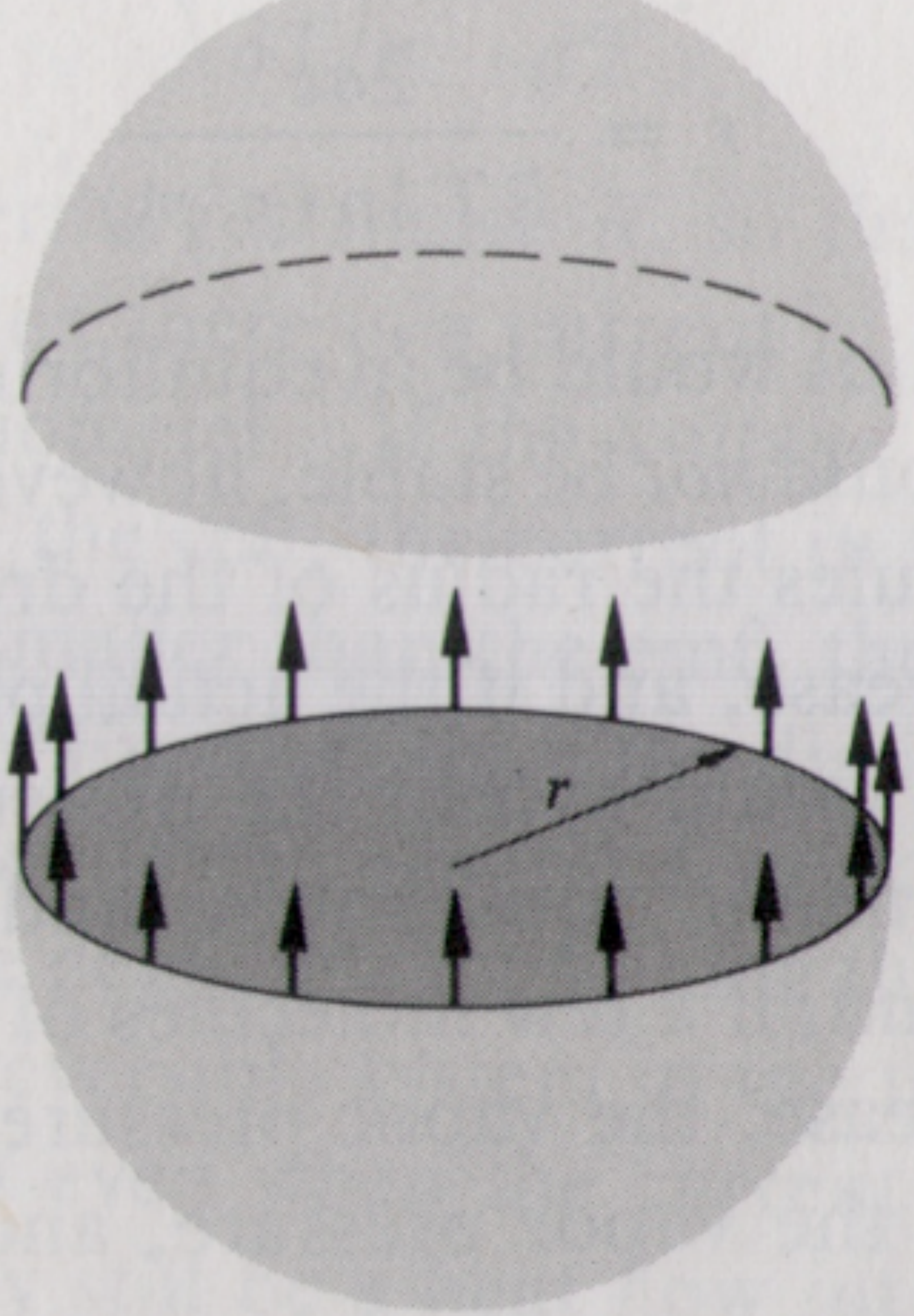


Fig. 8–3 Surface tension forces in a spherical drop.

For the mechanical equilibrium

$$(P_{\rm int} - P_{\rm ext})\pi r^2 = 2\pi r\sigma$$
$$\Rightarrow \quad P_{\rm int} - P_{\rm ext} = \frac{2\sigma}{r}$$

For thermodynamical equilibrium

$$\ln\frac{p}{p_0} = \frac{v''}{RT}(P_{\rm int} - p_0)$$
$$= \frac{v''}{RT}\left[p - p_0 + \frac{2\sigma}{r}\right]$$

In practice $p - p_0 \ll \frac{2\sigma}{r}$

$$\Rightarrow \quad \ln\frac{p}{p_0} = \frac{2\sigma v''}{rRT} \quad \Rightarrow \quad r = \frac{2\sigma v''}{RT\ln\frac{p}{p_0}}$$

The equilibrium is not stable:

$$r \searrow \quad \Rightarrow p \nearrow \quad \Rightarrow \quad p > P_{\rm ext}$$
$$\Rightarrow \quad \text{drop would evaporate}$$

$$r \nearrow \quad \Rightarrow p \searrow \quad \Rightarrow \quad p < P_{\rm ext}$$
$$\Rightarrow \quad \text{drop would grow}$$

Thermodynamics of magnetism

$$\text{1st law}: \ \delta W = PdV - HdM$$

For paramagnetic chrystals $PdV \ll \mathcal{H}dM \Rightarrow \delta W = -\mathcal{H}dM$

Magnetic potential energy $E_p = -\mathcal{H}M$

$\Rightarrow$ total energy $E = U + E_p = U - \mathcal{H}M$

$$\left.\begin{aligned} dE &= dU - \mathcal{H}dM - Md\mathcal{H} \\ TdS &= dU + \delta W = dU - \mathcal{H}dM \end{aligned}\right\} \Rightarrow TdS = dE + Md\mathcal{H}$$

For PVT systems $TdS = dH - VdP \Rightarrow$ E is a "magnetic enthalpy"

Physics is different, but equations have the same form

$\Rightarrow$ we can replace $H \to E$, $V \to -M$, $P \to \mathcal{H}$

Analog of c_P : $c_{\mathcal{H}} \equiv \left(\frac{\partial E}{\partial T}\right)_{\mathcal{H}}$, analog of c_V : $c_M \equiv \left(\frac{\partial U}{\partial T}\right)_M$

TdS equations :

$$\begin{cases} TdS = c_M dT - T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M dM, \\ TdS = c_{\mathcal{H}} dT + T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} d\mathcal{H} \end{cases}$$

We defined $F^* = E - TS$

$$\left.\begin{array}{rcl} dF^* &=& dE - TdS - SdT \\ TdS &=& dE + Md\mathcal{H} \end{array}\right\} \Rightarrow \quad dF^* = -SdT - Md\mathcal{H}$$

$$\Rightarrow \quad \left(\frac{\partial F^*}{\partial T}\right)_{\mathcal{H}} = -S, \qquad \left(\frac{\partial F^*}{\partial \mathcal{H}}\right)_T = -M$$

Statistical thermodynamics $\Rightarrow \quad F^* = F^*(T, \mathcal{H})$

$\Rightarrow$ the second eqn is the *magnetic equation of state*

Energy equation:

$$U = E + \mathcal{H}M = F^* + TS + \mathcal{H}M = F^* - T\left(\frac{\partial F^*}{\partial T}\right)_{\mathcal{H}} - \mathcal{H}\left(\frac{\partial F^*}{\partial \mathcal{H}}\right)_T$$

$\Rightarrow$ All properties of the magnetic system are defined by $F^*(T, \mathcal{H})$

"Maxwell equation" $\Rightarrow \quad \left(\frac{\partial S}{\partial \mathcal{H}}\right)_T = \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}$

For a paramagnetic obeying Curie's law $\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} < 0$

$\Rightarrow$ the entropy decreases as the magnetic intensity increases

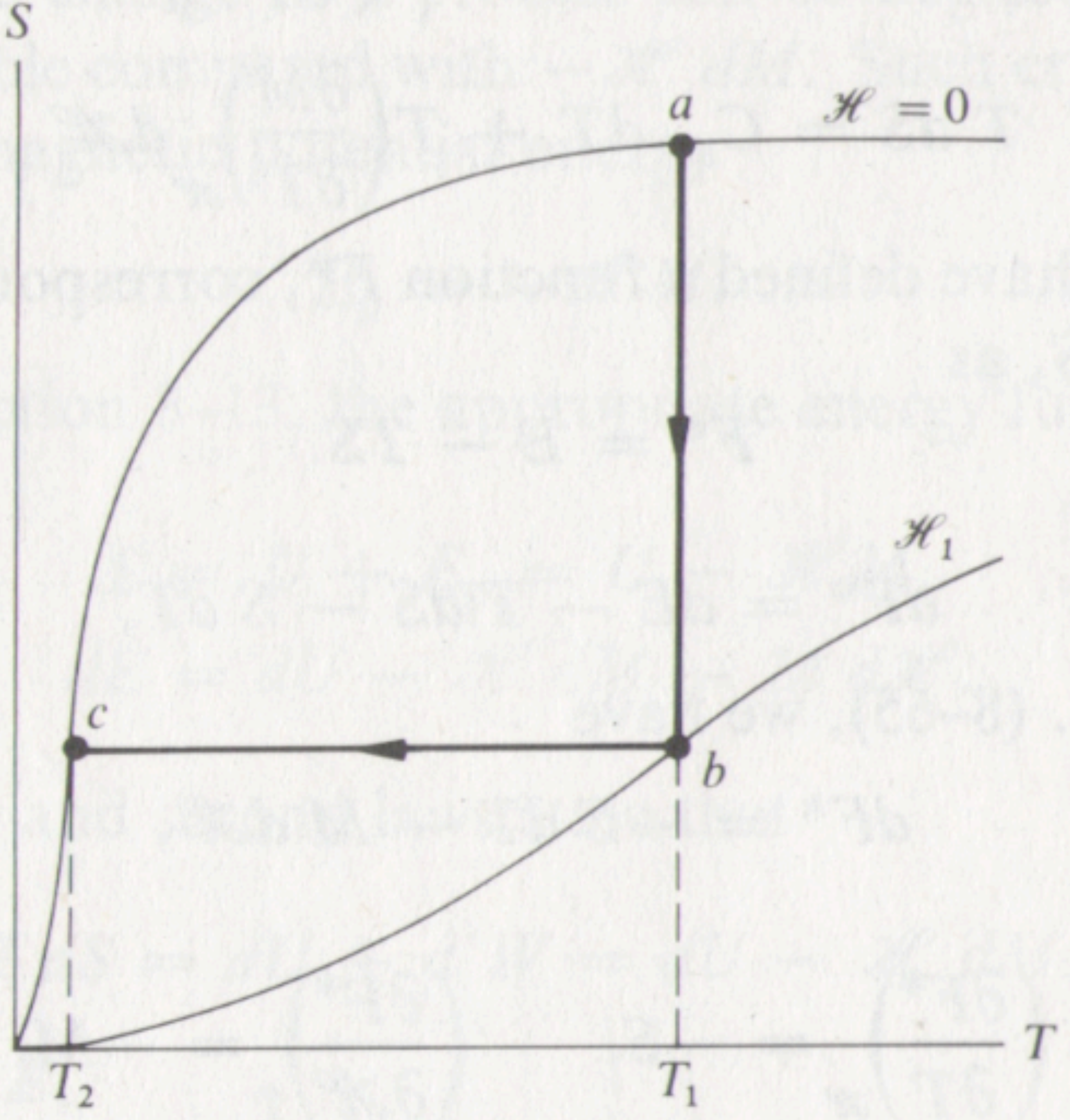


Fig. 8–4 The temperature dependence of the entropy of a magnetic system at $\mathscr{H} = 0$ and at $\mathscr{H} = \mathscr{H}_1$.

From Nernst theorem

$$\left(\frac{\partial S}{\partial \mathcal{H}}\right)_T \overset{T\to 0}{\to} 0$$

$$\Rightarrow \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} \overset{T\to 0}{\to} 0$$

⇒ Curie's law $M = C_C \frac{\mathcal{H}}{T}$

cannot hold at $T = 0$

⇒ phase transition as $T \to 0$

Adiabatic demagnetization

$a \to b$: isothermal increase of $\mathcal{H}$

⇒ heat flows out

$$\delta Q_T = T dS_T = T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} d\mathcal{H}_T$$

$b \to c$: adiabatic decrease of $\mathcal{H}$

$$0 = TdS = c_{\mathcal{H}} dT + T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} d\mathcal{H}$$

$$\Rightarrow dT_S = -\frac{T}{C_{\mathcal{H}}}\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} d\mathcal{H}_s$$

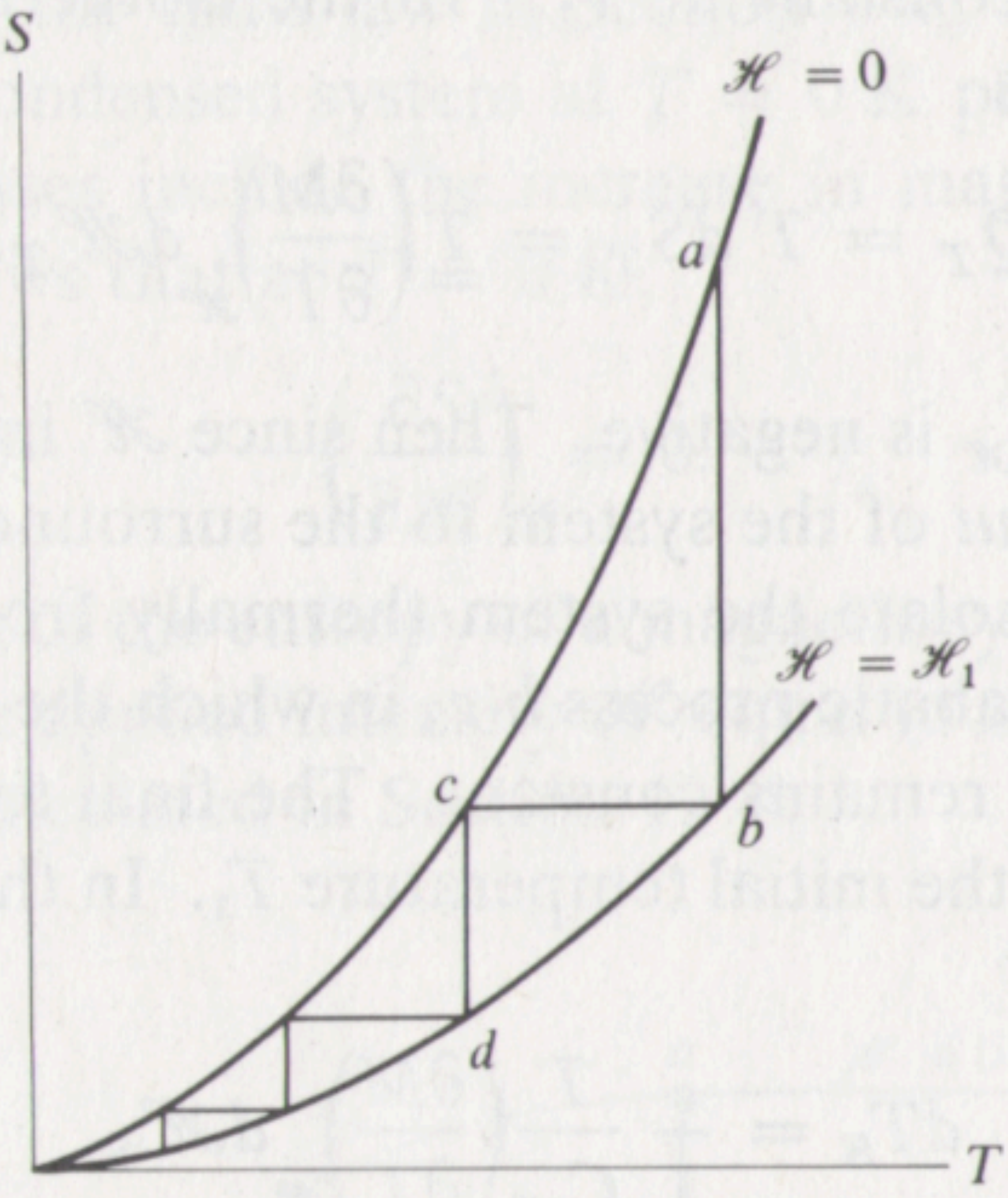
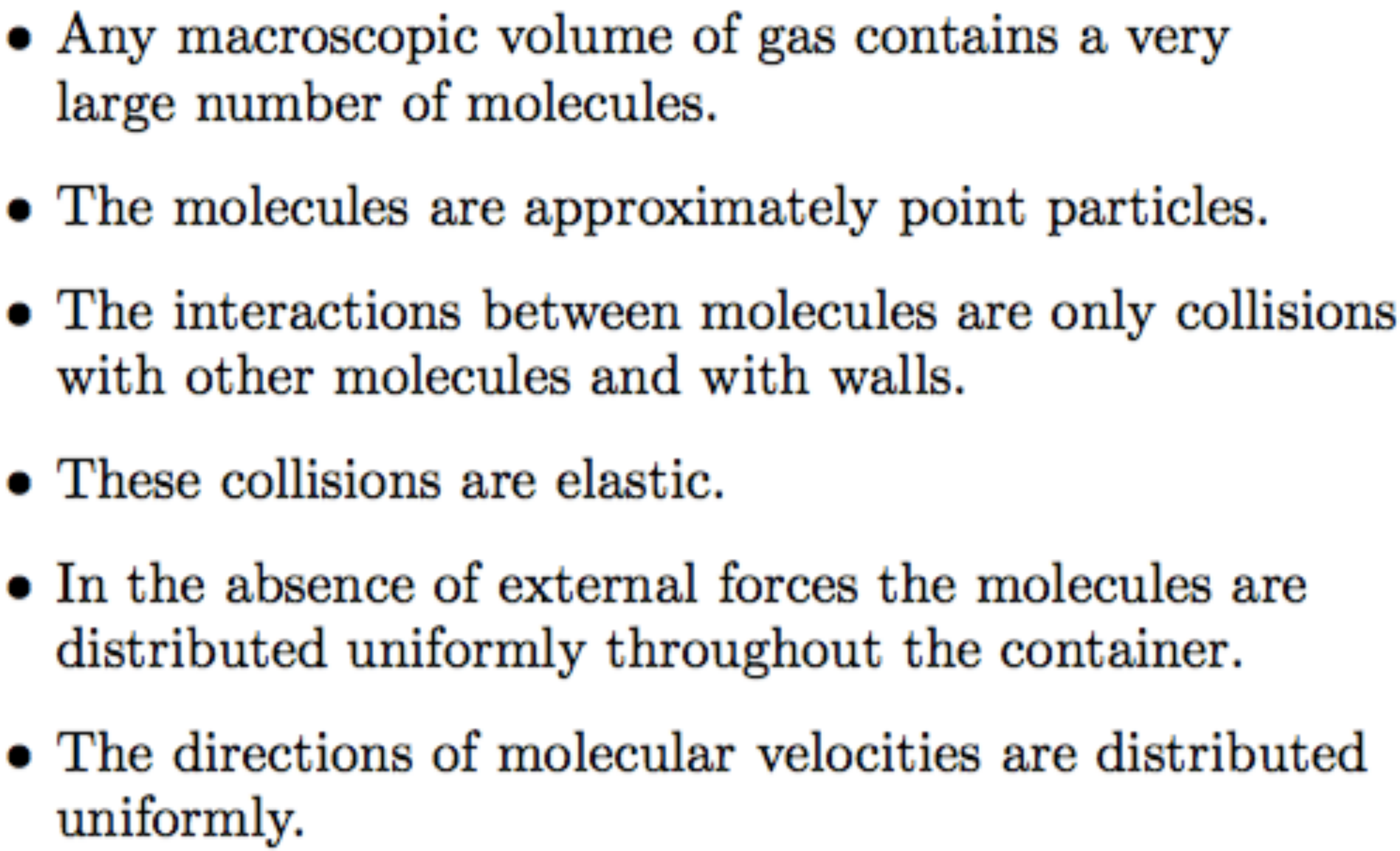


Fig. 8–5 The unattainability of the absolute zero of temperature by a finite series of isothermal magnetizations and adiabatic demagnetizations.

It is possible to prove that if the entropy is not 0 at T=0 for H=0, the absolute zero of temperature could be reached in a finite number of processes in violation of the unattainability statement of 3rd law

Kinetic theory of ideal gases

Basic assumptions



- Any macroscopic volume of gas contains a very large number of molecules.
- The molecules are approximately point particles.
- The interactions between molecules are only collisions with other molecules and with walls.
- These collisions are elastic.
- In the absence of external forces the molecules are distributed uniformly throughout the container.
- The directions of molecular velocities are distributed uniformly.

Uniform distribution of directions of velocities

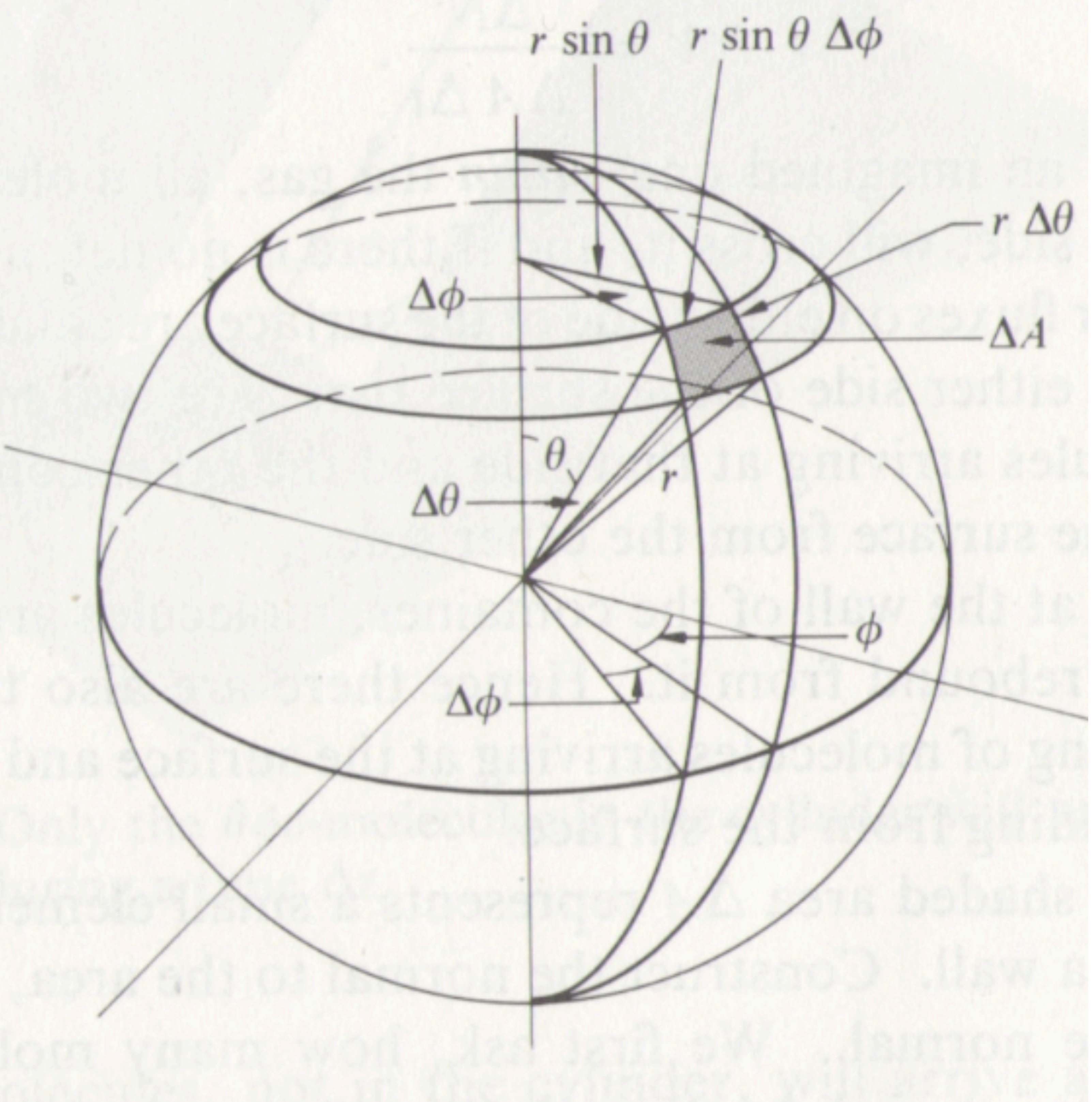


Fig. 9–1 Polar coordinates.

Ω – solid angle

$$\Delta A = r^2 \sin\theta\Delta\theta\Delta\phi \quad \Rightarrow$$

$$\Delta\Omega \equiv \frac{\Delta A}{r^2} = \sin\theta\Delta\theta\Delta\phi$$

The number of velocities pointing in $\Delta\Omega$ is

$$\Delta N = \frac{N}{4\pi}\Delta\Omega$$

$\Rightarrow$ the number density of molecules with velocities pointing in $\Delta\Omega$ is

$$\Delta n_\Omega = \frac{n}{4\pi}\Delta\Omega$$

$\Delta N_v \equiv$ the number of molecules with *speeds* between v and $v + \Delta v$

Molecular flux

$$\Phi \equiv \frac{\Delta N}{\Delta A \Delta t} = \text{total number of molecules arriving at the surface}$$

If the surface is inside: two fluxes - flux in and flux out.
If the surface is on the boundary, incoming flux and reflected flux.

Space – saving notation :
$\theta\phi v$ molecule $\equiv$ molecule with direction of velocity between
$\theta, \theta + d\theta$ and $\phi, \phi + d\phi$ and speed between $v, v + dv$

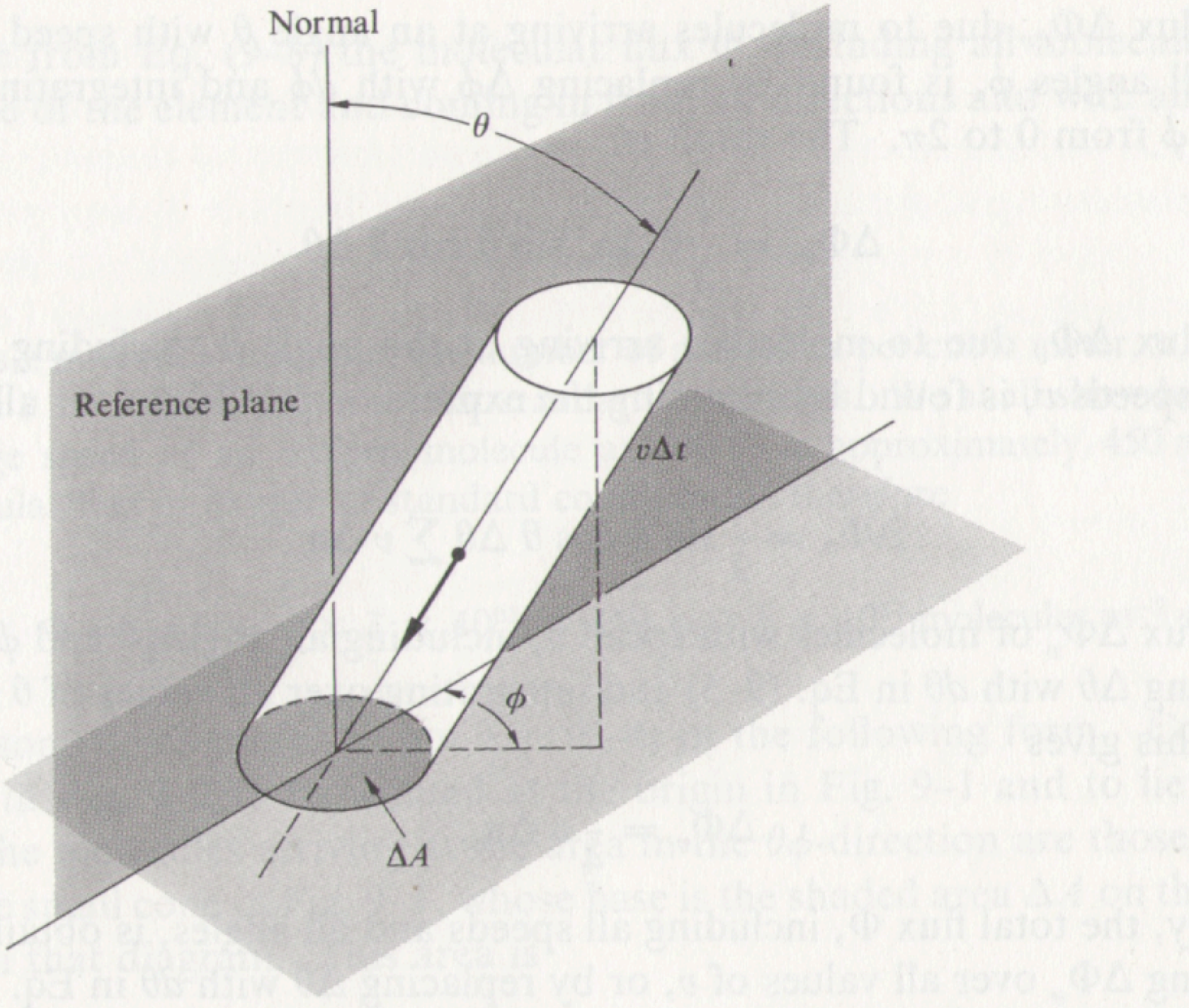


Fig. 9–2 Only the $\theta\phi v$-molecules in the cylinder will arrive at the area ΔA during a time Δt.

← the cylinder with axis in θ, ϕ direction and length $v\Delta t$

The number of $\theta\phi v$ molecules that arrive at the surface during Δt = the number of molecules in the cylinder

$$\left.\begin{array}{l}\text{The number density of } \theta\phi v \text{ molecules is} \frac{\Delta n_v}{4\pi}\sin\theta d\theta d\phi \\ \text{the volume of slant cylinder is } \Delta V \;=\; (\Delta A\cos\theta)(v\Delta t)\end{array}\right\} \Rightarrow$$

$$\Rightarrow \left\{\begin{array}{l}\text{the number of } \theta\phi v \text{ molecules in the cylinder is} \\ \Delta N_{\theta\phi v} \;=\; \frac{v}{4\pi}\Delta n_v \sin\theta\cos\theta\Delta\theta\Delta\phi\Delta A\Delta t \;\Rightarrow \\ \;\Rightarrow\quad \text{the flux of } \theta\phi v \text{ molecules is} \\ \Delta\Phi_{\theta\phi v} \;=\; \frac{v}{4\pi}\Delta n_v \sin\theta\cos\theta\Delta\theta\Delta\phi\end{array}\right.$$

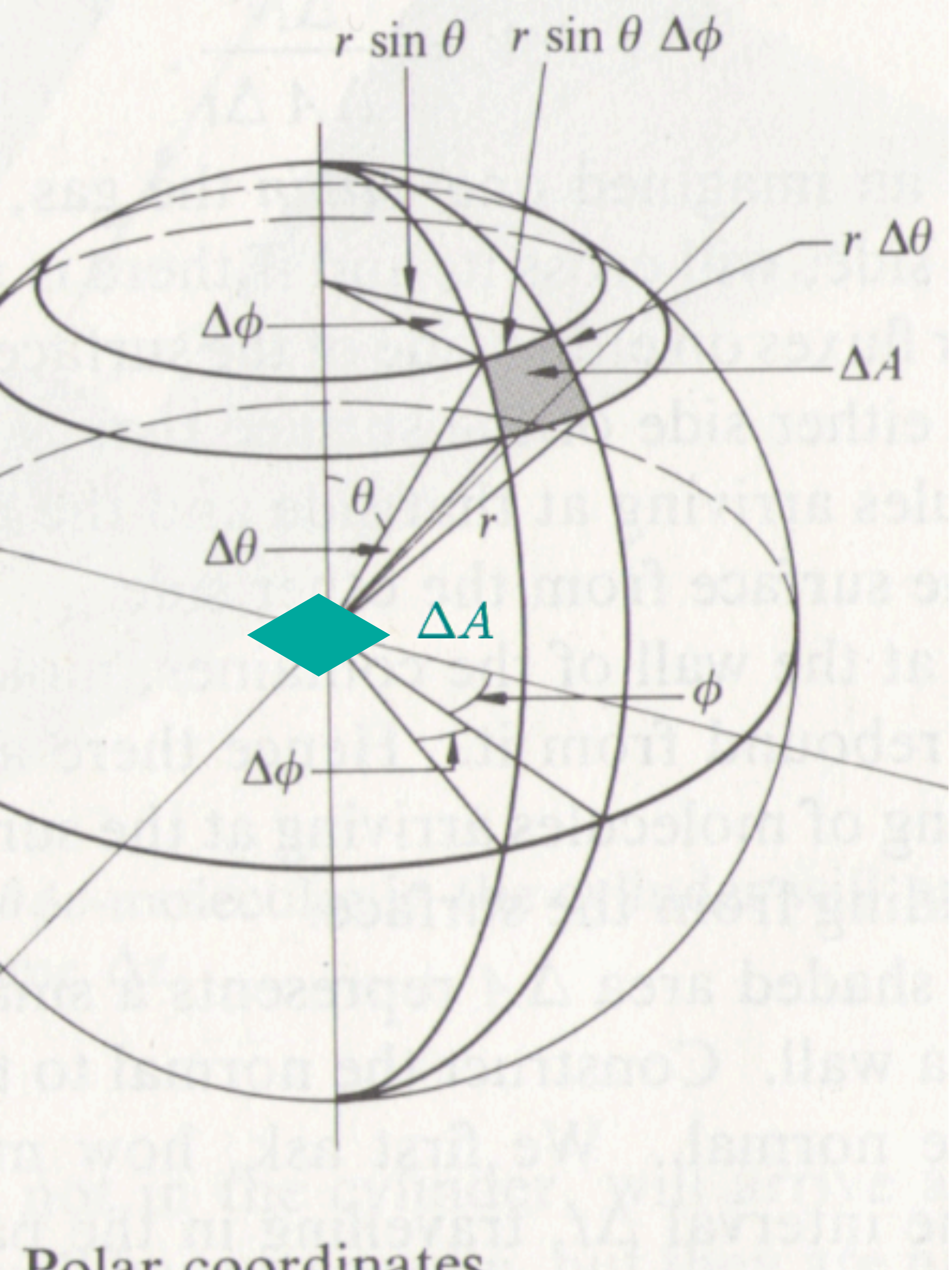
For all azimuthal angles $\Delta\Phi_{\theta v} \;=\; 2\pi\Delta\Phi_{\theta\phi v} \;=\; \frac{v}{2}\Delta n_v \sin\theta\cos\theta\Delta\theta$

$\Rightarrow$ for all angles θ and ϕ $\Delta\Phi_v \;=\; \int_0^{\pi/2}\Delta\Phi_{\theta\phi v} \;=\; \frac{v}{4}\Delta n_v$

$\Rightarrow$ the total flux is $\Phi \;=\; \frac{1}{4}\sum v\Delta n_v$

Average velocity : $\bar{v} \;\equiv\; \frac{1}{N}\sum v \;=\; \frac{1}{N}\sum v\Delta n_v$

$$\Rightarrow \;\Phi \;=\; \frac{1}{4}\bar{v}n$$



Polar coordinates

The molecules arriving at the area in the $\theta\phi$ direction are those coming from the small cone whose base is ΔA on the spherical surface

$$\begin{aligned} \Delta\Phi_{\theta\phi v} &= \\ &= \frac{1}{4\pi}\Delta n_v \sin\theta\cos\theta\Delta\theta\Delta\phi \\ &= \frac{\cos\theta}{4\pi}\Delta n_v d\Omega \end{aligned}$$

$$\Rightarrow \quad \frac{\Delta\Phi_{\Omega v}}{\Delta\Omega} = \frac{1}{4\pi}\Delta n_v \cos\theta$$

The greatest number of molecules arrives from the cone centered at the normal

Equation of state of an ideal gas

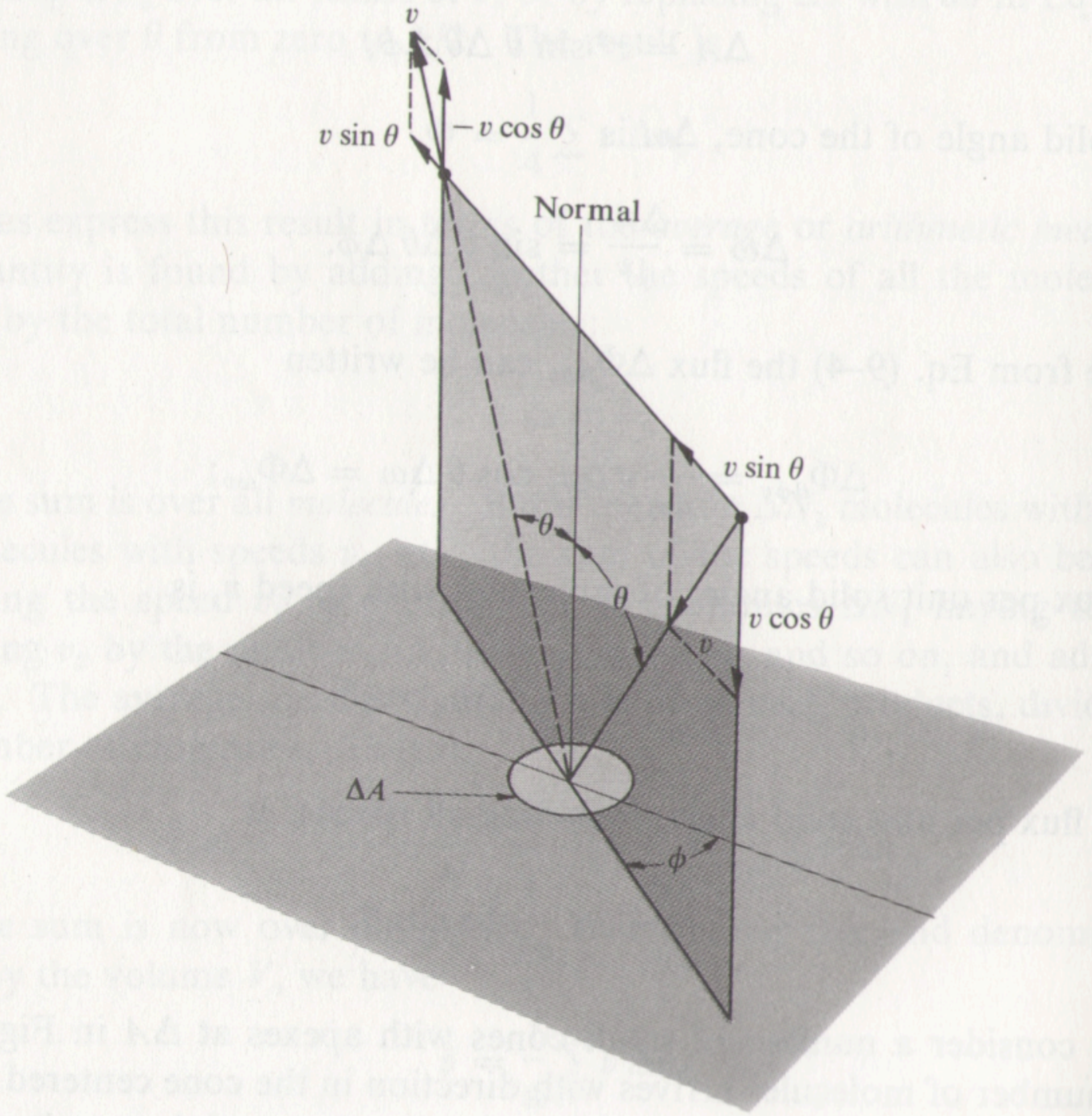


Fig. 9–3 Change in velocity in an elastic collision.

Change of momentum :

$$\Delta p \ = \ 2mv\cos\theta$$

Flux of θv molecules

$$\Delta\Phi_{\theta v} \ = \ \frac{\Delta n_v}{2}\sin\theta\cos\theta\Delta\theta$$

Pressure due to θv molecules

$$\Delta P_{\theta\phi} \ = \ \Delta\Phi_{\theta v} 2mv\cos\theta$$

$$= \ mv^2\Delta n_v \sin\theta\cos^2\theta\Delta\theta$$

Pressure due to all molecules with speed v

$$\Delta\Phi_{\theta v} \ = \ \frac{mv^2}{3}\Delta n_v$$

$$\Rightarrow \quad P \ = \ \frac{1}{3}m\sum v^2\Delta n_v$$

This formula is also correct for any surface inside the gas

Mean square speed : $\overline{v^2} \equiv \frac{1}{N}\sum v^2 = \frac{1}{N}\sum v^2 \Delta N_v = \frac{1}{n}\sum v^2 \Delta n_v$

$$\sum v^2 \Delta n_v = n\overline{v^2} \quad \Rightarrow \quad P = \frac{1}{3}nm\overline{v^2}$$

Comparing to equation of an ideal gas $PV = NkT$ we get $\overline{v^2} = \frac{3kT}{m}$

$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$ ← mean kinetic energy of a molecule is proportional to T

Collisions with a moving wall

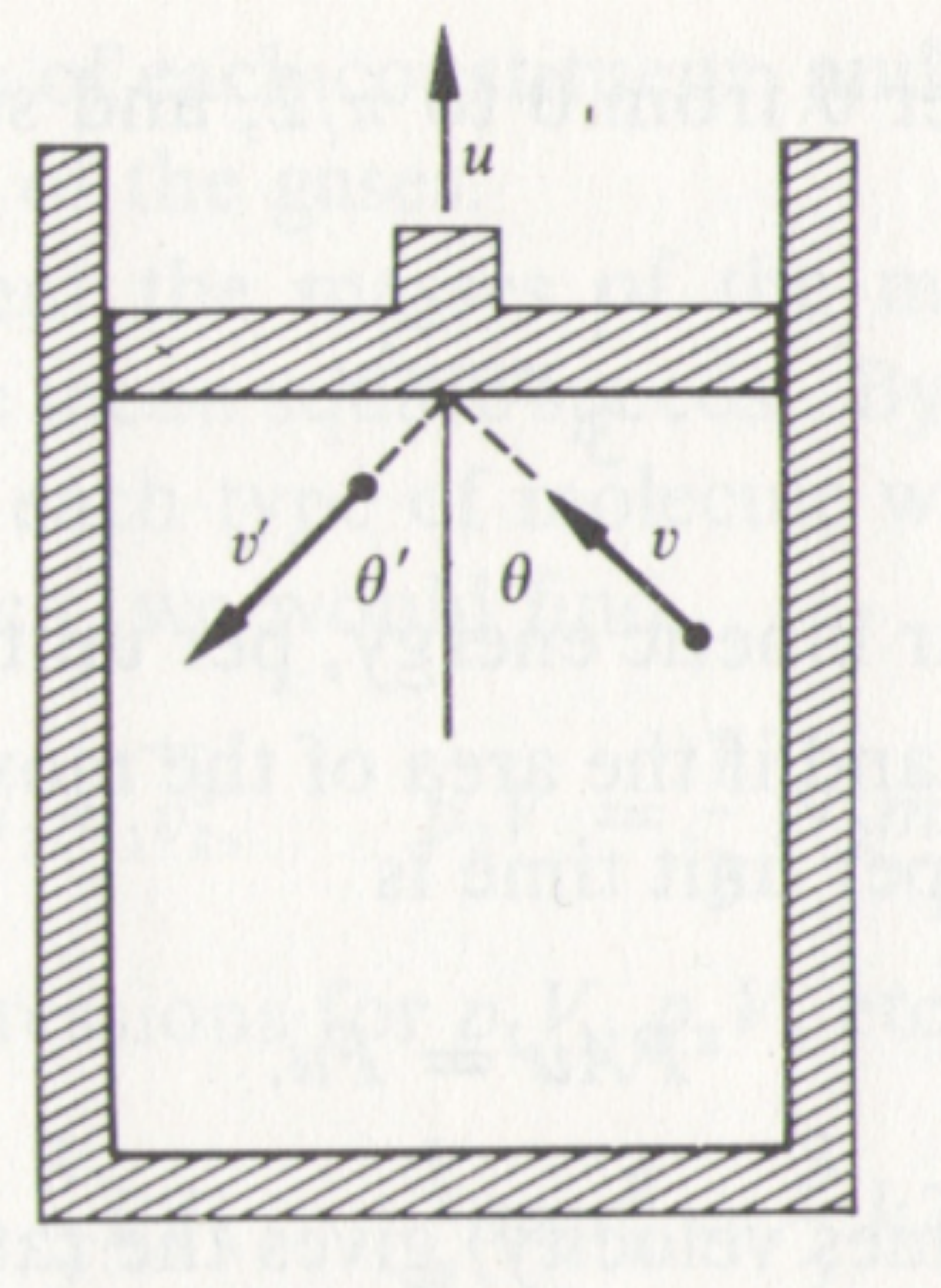


Fig. 9–4 Collisions with a moving wall.

$u \ll v \;\Rightarrow$

the loss of kinetic energy of molecule

$$m\frac{(v\cos\theta)^2}{2} - m\frac{(v\cos\theta - 2u)^2}{2} \;=\; 2mvu\cos\theta$$

$\Rightarrow$ Loss of molecular kinetic energy per unit area per unit time due to θv collisions

$= \; muv^2 \Delta n_v \sin\theta\cos\theta\Delta\theta$

$\Rightarrow$ Total loss of molecular kinetic energy per unit area per unit time

$= \; \frac{1}{3}mu\overline{v^2} \;=\; Pu$

Rate at which mechanical work is done on the piston

$= \; Fu \;=\; PAu$

$=$ rate of decrease of molecular kinetic energy

Equipartition of energy

Consider mixture of ideal gases

Experimental fact (***Dalton's law***):
total pressure is the sum of partial pressures.

$$p_1V = N_1kT, \quad p_2V = N_2kT, \ \ldots \qquad p_i \equiv partial \ pressure$$

From previous lecture : $p_1V = \frac{1}{3}N_1m_1\overline{v_1^2}, \ p_2V = \frac{1}{3}N_2m_2\overline{v_2^2}, \ldots$

$$\Rightarrow \frac{1}{2}m_1\overline{v_1^2} = \frac{3}{2}kT, \quad \frac{1}{2}m_2\overline{v_2^2} = \frac{3}{2}kT, \ldots$$

In a mixture mean kinetic energies of molecules of each gas are the same

$$\left.\begin{array}{l} \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} \Rightarrow \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{\overline{v^2}}{3} \\ \Rightarrow \frac{1}{2}m\overline{v_x^2} = \frac{1}{2}m\overline{v_y^2} = \frac{1}{2}m\overline{v_z^2} = \frac{1}{2}kT \end{array}\right\} \Rightarrow \ \frac{1}{2}kT \text{ for each } \textit{degree of freedom}$$

If energy is a quadratic function of variables $\Rightarrow \frac{1}{2}kT$ for each degree of freedom

Total energy of N molecules with f degrees of freedom $= \frac{N}{2}NkT = \frac{f}{2}nRT$

Classical theory of specific heat capacity

The internal energy of an ideal gas $U = \frac{f}{2} NkT = \frac{f}{2} nRT$

$$u = \frac{f}{2} RT \quad \Rightarrow \quad c_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{f}{2} R$$

Monoatomic gas $c_v = \frac{3}{2}R, \quad c_P = c_v + R = \frac{5}{2}R, \quad \gamma = \frac{c_P}{c_v} = \frac{5}{3} \sim 1.6$

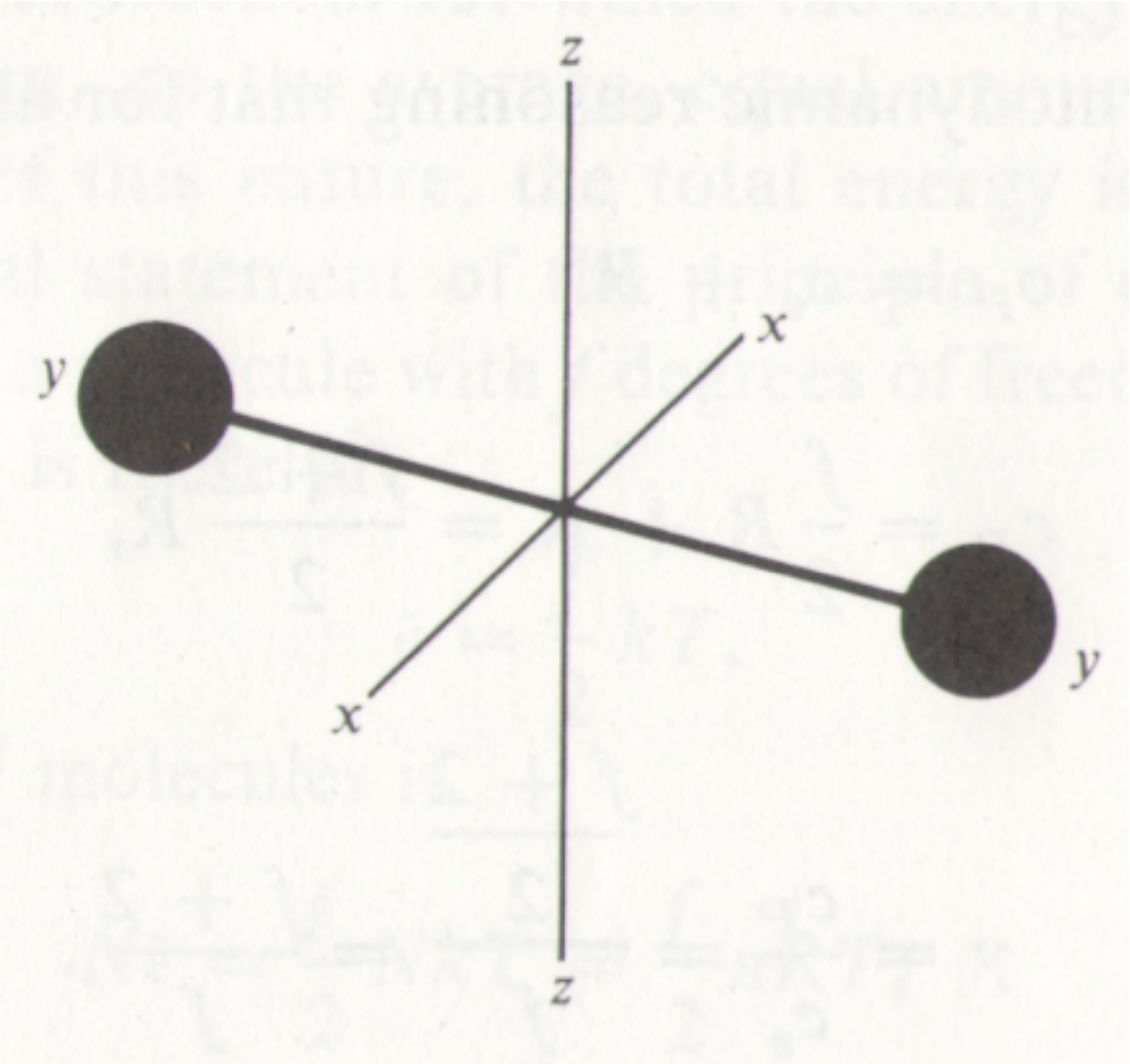


Fig. 9–5 A dumbbell molecule.

$I_x = I_z \gg I_y \quad \Rightarrow$ effectively two rotational degrees of freedom

Two vibrational degrees of freedom :

$E_{\text{kin}} = F(\text{velocity})$ and

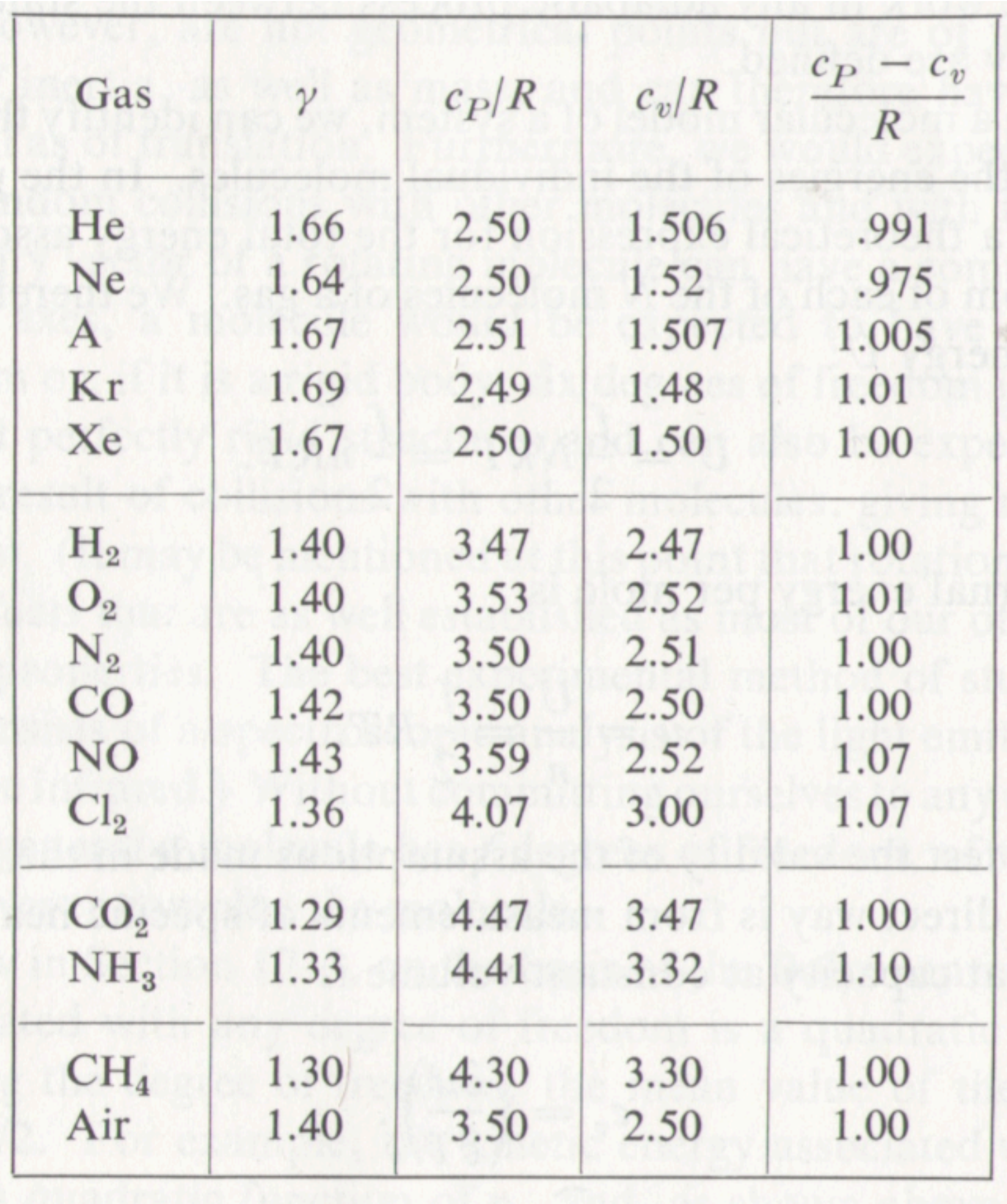
$E_{\text{pot}} = F(\text{separation})$

$\Rightarrow$ for a diatomic molecule

$f = 7 \;\rightarrow\; c_v = \frac{7}{2}R,$

$c_P = \frac{9}{2}R, \quad \gamma = \frac{9}{7} \simeq 1.29$

Heat capacities of monoatomic and diatomic gases near room *T*



Gas	γ	c_P/R	c_v/R	$\frac{c_P - c_v}{R}$
He	1.66	2.50	1.506	.991
Ne	1.64	2.50	1.52	.975
A	1.67	2.51	1.507	1.005
Kr	1.69	2.49	1.48	1.01
Xe	1.67	2.50	1.50	1.00
H_2	1.40	3.47	2.47	1.00
O_2	1.40	3.53	2.52	1.01
N_2	1.40	3.50	2.51	1.00
CO	1.42	3.50	2.50	1.00
NO	1.43	3.59	2.52	1.07
Cl_2	1.36	4.07	3.00	1.07
CO_2	1.29	4.47	3.47	1.00
NH_3	1.33	4.41	3.32	1.10
CH_4	1.30	4.30	3.30	1.00
Air	1.40	3.50	2.50	1.00

Monoatomic :

$$\frac{c_v}{R} = \frac{3}{2}, \quad \frac{c_P}{R} = \frac{5}{2},$$

$$\gamma = \frac{c_P}{c_v} \simeq 1.67$$

Diatomic :

$$\frac{c_v}{R} = \frac{7}{2}, \quad \frac{c_P}{R} = \frac{9}{2},$$

$$\gamma = \frac{c_P}{c_v} \simeq 1.29$$

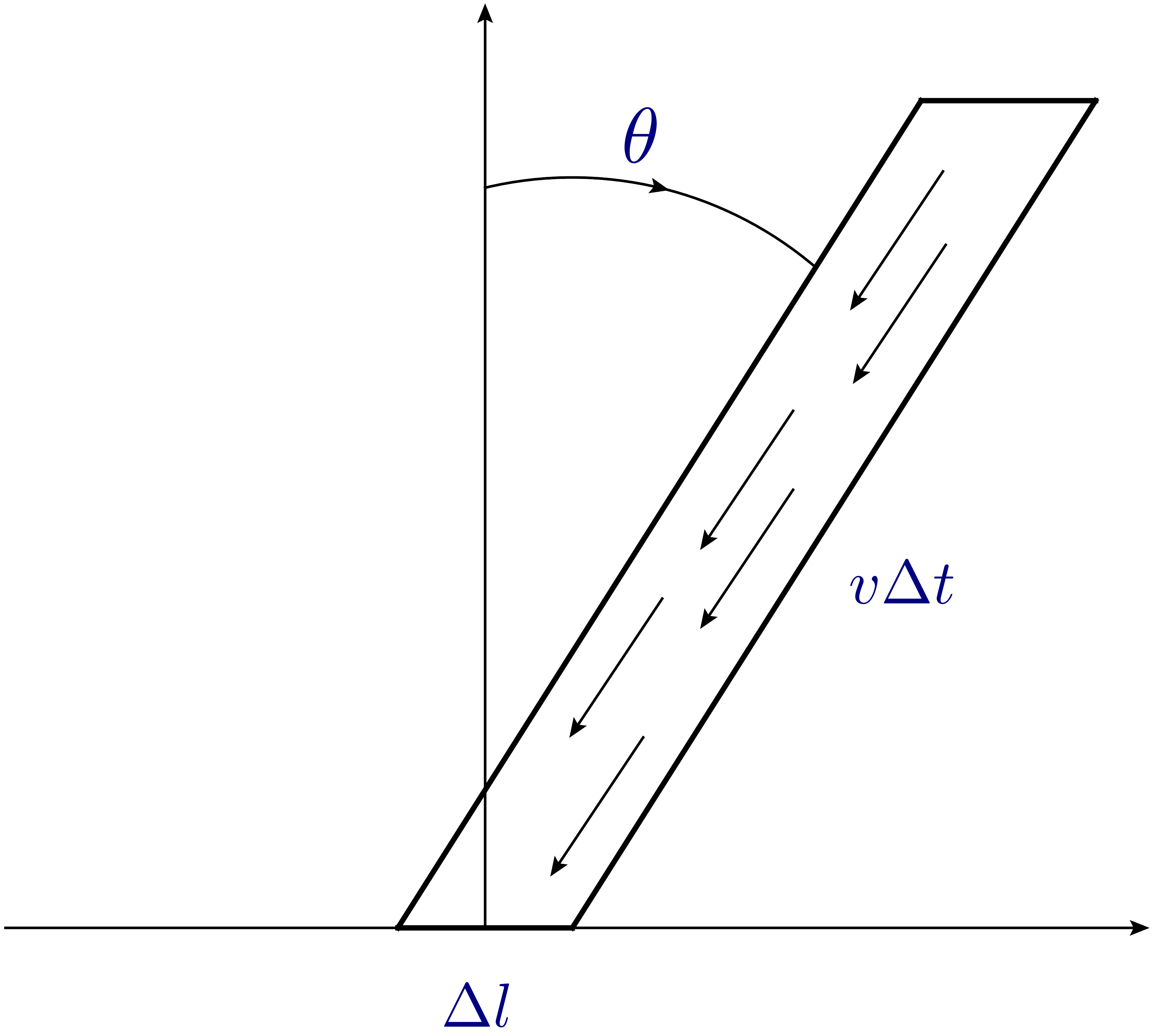
The pressure depends on the translational kinetic energy

$$U_{\mathrm{tr}} = \frac{3}{2} NkT$$

$$\Rightarrow \quad P = \frac{2}{3}\frac{U_{\mathrm{tr}}}{V}$$

$$= \frac{2}{3} u_{\mathrm{tr}} = \frac{1}{v} RT$$

Problem 9-10: ideal gas in two dimensions



$\leftarrow$ the rhombus with axis in θ direction and length $v\Delta t$

The number of θv molecules arriving at Δl during Δt $=$

$=$ the number of molecules in the rhombus

$$\left.\begin{array}{l}\text{The number density of } \theta v \text{ molecules is} \frac{\Delta n_v}{2\pi} d\theta \\ \text{the area of rhombus is } \Delta A \;=\; (\Delta l \cos\theta)(v\Delta t)\end{array}\right\} \Rightarrow$$

$$\Rightarrow \left\{\begin{array}{l}\text{the number of } \theta v \text{ molecules in the rhombus is} \\ \Delta N_{\theta v} \;=\; \frac{v}{2\pi}\Delta n_v \cos\theta \Delta\theta \Delta l \Delta t \;\Rightarrow \\ \;\Rightarrow\quad \text{the “flux}'' \text{ of } \theta v \text{ molecules is} \\ \Delta\tilde{\Phi}_{\theta v} \;=\; \frac{v}{2\pi}\Delta n_v \cos\theta\Delta\theta\end{array}\right.$$

$$\text{for all angles } \theta \quad \Delta\tilde{\Phi}_v \;=\; \int_{-\pi/2}^{\pi/2} \Delta\tilde{\Phi}_{\theta v}\, d\theta \;=\; \frac{v}{\pi}\Delta n_v$$

$$\Rightarrow \quad \text{the total flux is} \quad \tilde{\Phi} \;=\; \frac{1}{\pi}\sum v\Delta n_v$$

$$\text{Average velocity}: \;\; \bar{v} \;\equiv\; \frac{1}{N}\sum v \;=\; \frac{1}{N}\sum v\Delta n_v$$

$$\Rightarrow \; \tilde{\Phi} \;=\; \frac{1}{\pi}\bar{v}n$$

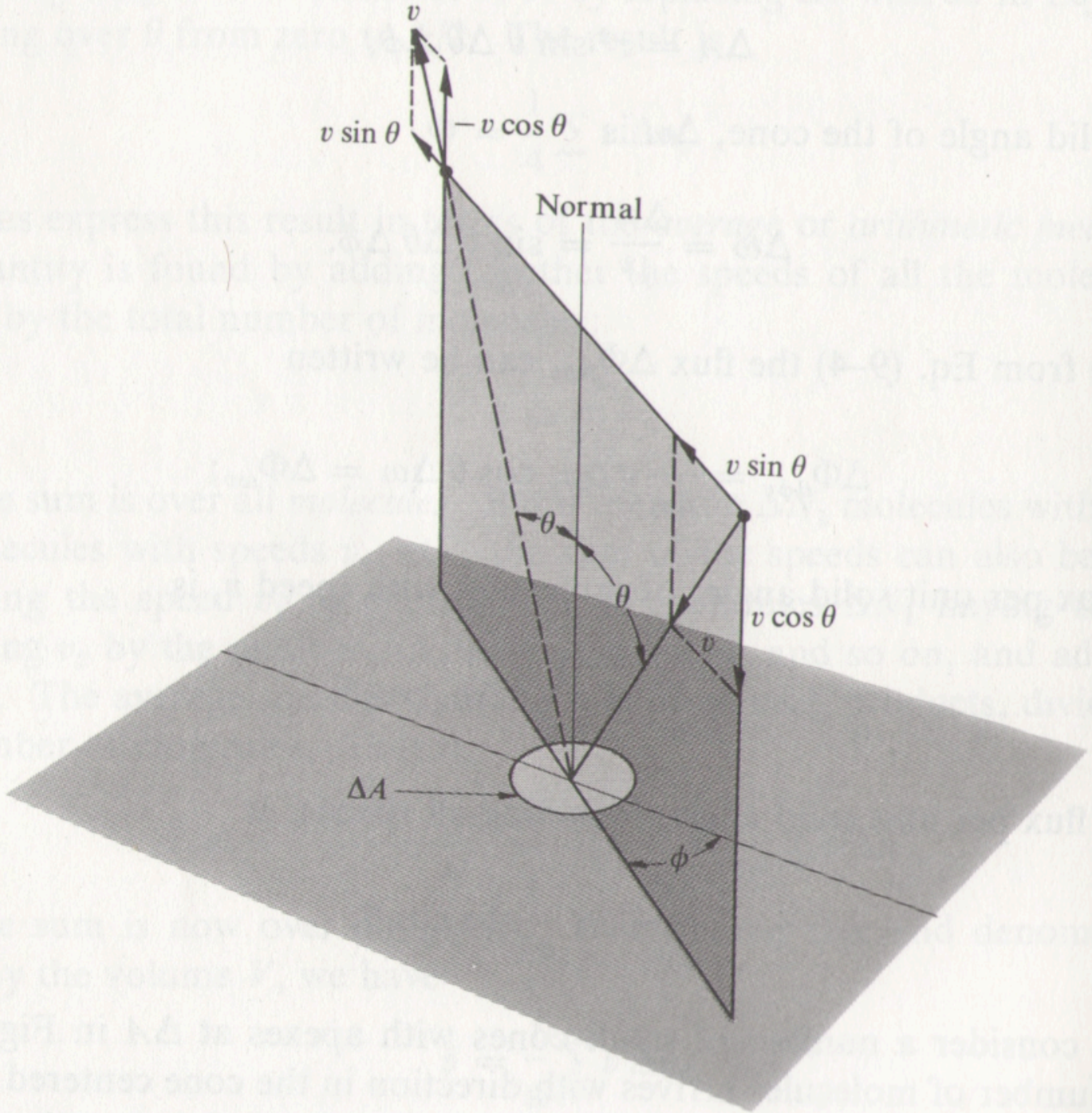


Fig. 9–3 Change in velocity in an elastic collision.

Change of momentum :

$$\Delta p \; = \; 2mv\cos\theta$$

Flux of θv molecules

$$\Delta\tilde{\Phi}_{\theta v} \; = \; \frac{v}{2\pi}\Delta n_v \cos\theta\Delta\theta$$

"Pressure" due to θv molecules

$$\Delta\tilde{P}_{\theta v} \; = \; \Delta\tilde{\Phi}_{\theta v} 2mv\cos\theta$$

$$= \; \frac{mv^2}{\pi}\Delta n_v \cos^2\theta\Delta\theta$$

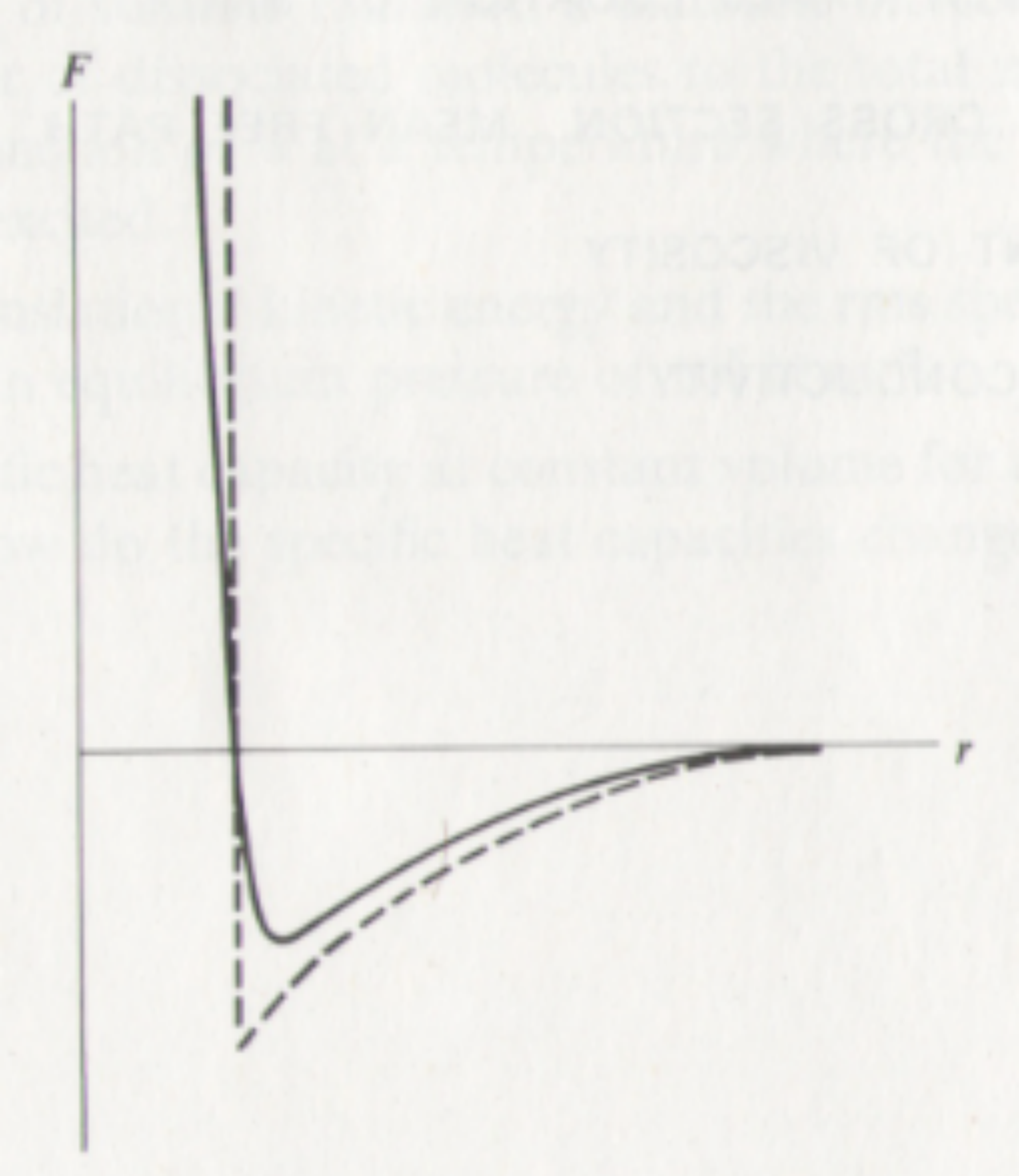
"Pressure" due to all molecules with speed v

$$\Delta\tilde{P}_v \; = \; \frac{mv^2}{2}\Delta n_v$$

$$\Rightarrow \quad \tilde{P} \; = \; \frac{1}{2}m\sum v^2\Delta n_v$$

$$\Rightarrow \quad \tilde{P} \; = \; \frac{1}{2}nm\overline{v^2}$$

Intermolecular forces. Transport phenomena



<- Typical intermolecular forces

Van der Waals equation of state

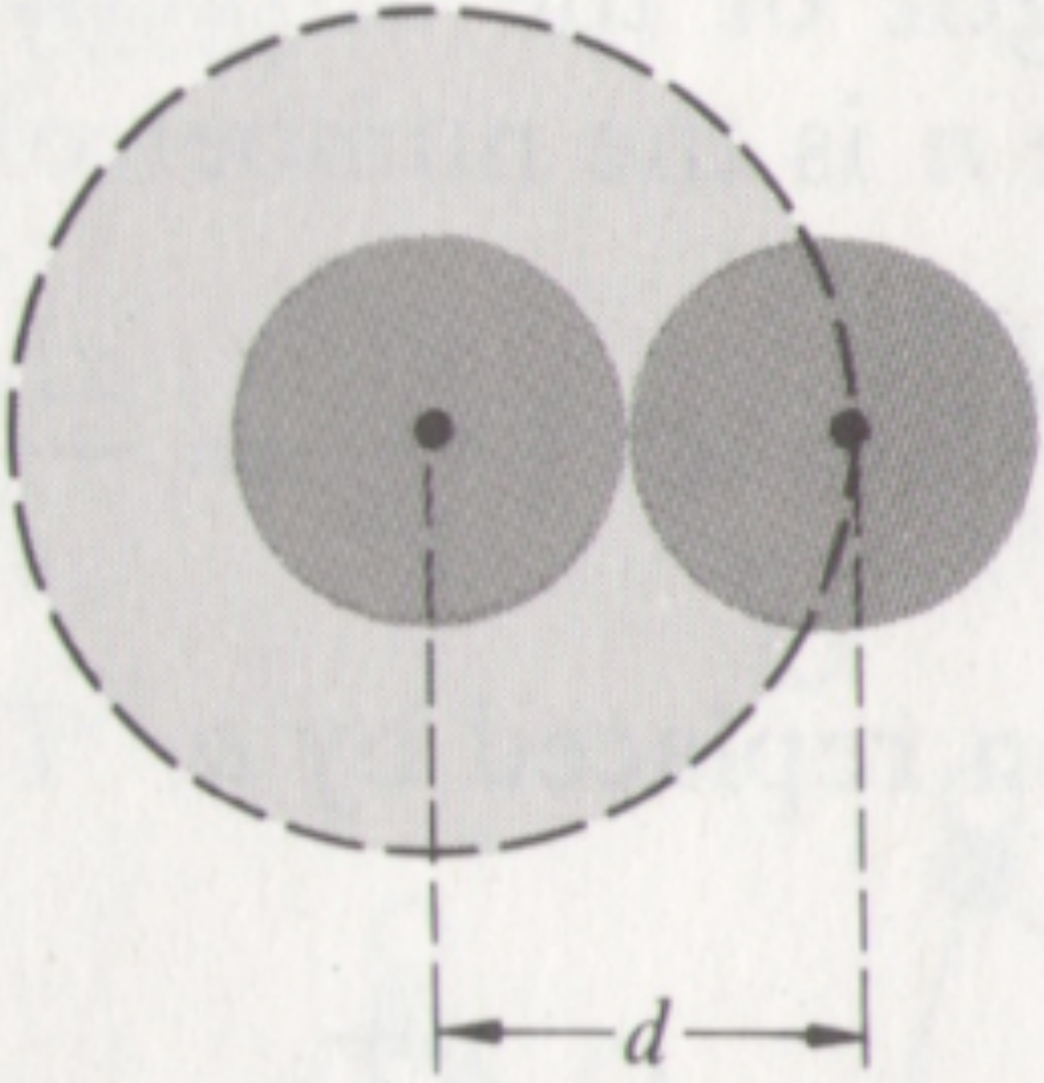


Fig. 10–2 The radius of the sphere of exclusion equals the molecular diameter *d*.

If we take into account ``available" volume for molecules

$$P(V - nb) = nRT$$

$$\Rightarrow P(v - b) = RT$$

Unavailable volume

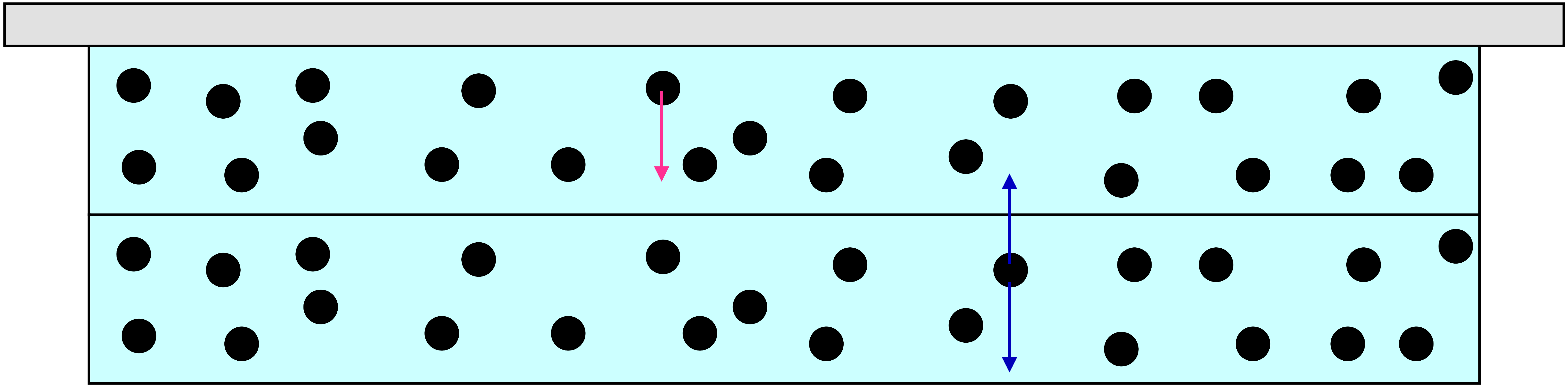
$$= \frac{N}{2} \times \frac{4}{3}\pi d^3$$

$$\Rightarrow b = \frac{2}{3} N_A \pi d^3$$

$$= 4(\text{volume of molecules})$$

Van der Waals correction

Assume rapidly decreasing attractive force between the molecules and assume the nearest-neighbor interaction



The force of attraction is proportional to number of molecules per unit volume in outer layer and to the density in the next-to-outer layer

The pressure $\frac{RT}{V-b}$ will be reduced by $\alpha\left(\frac{N}{V}\right)^2 = \alpha n^2 = \frac{\alpha N_A^2}{v^2} = \frac{a}{v^2}$

where $a = N_A^2\alpha$ is some constant

$$\Rightarrow \quad P = \frac{RT}{V-b} - \frac{a}{v^2} \quad \Leftrightarrow \quad \left(P + \frac{a}{v^2}\right)(v-b) = RT$$

Collision cross section & mean free path

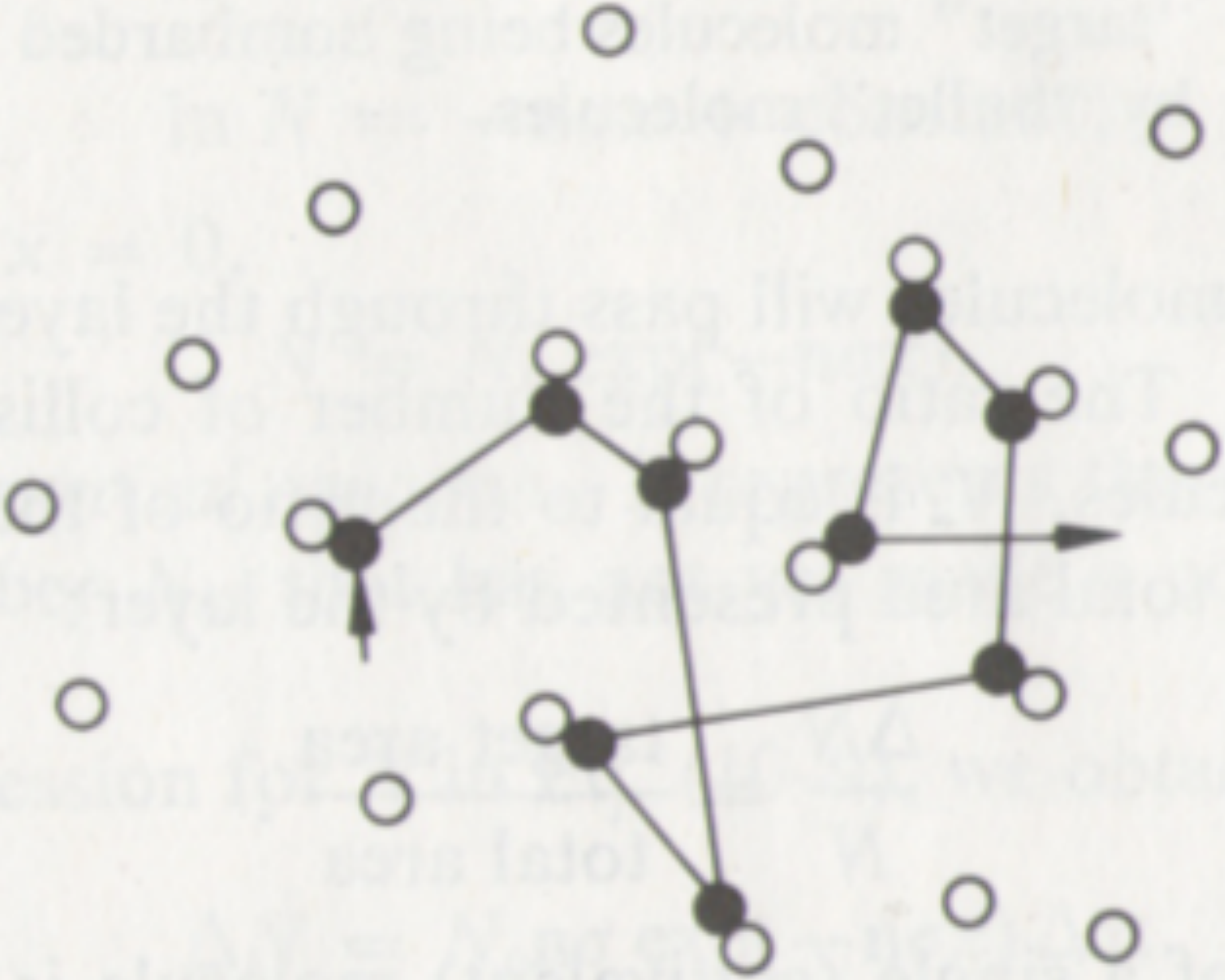


Fig. 10–3 Molecular free paths.

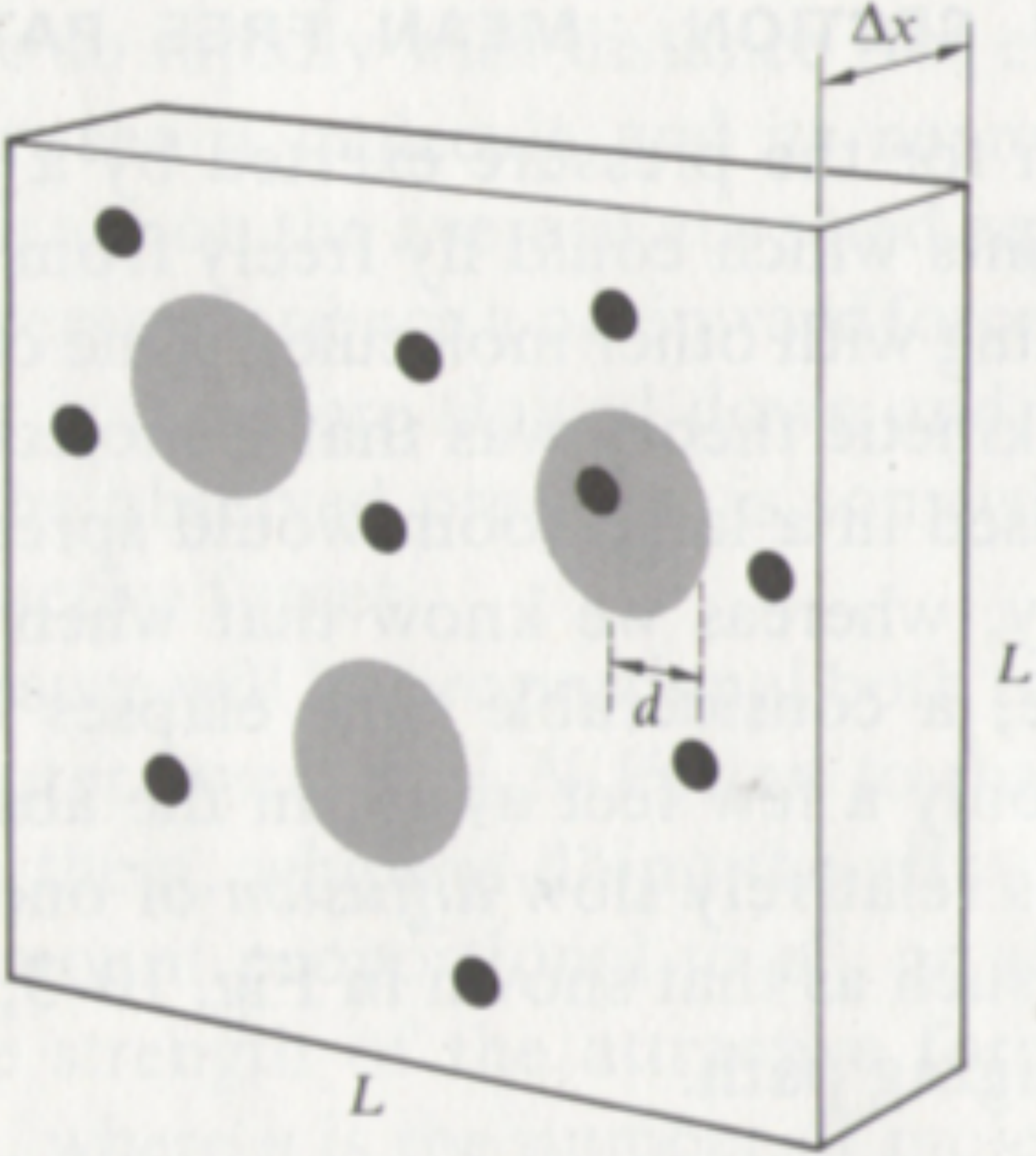


Fig. 10–4 A thin layer of gas of "target" molecules being bombarded by "bullet" molecules.

$$\frac{\Delta N_{\text{bullet}}}{N_{\text{bullet}}} = \frac{\text{target area}}{\text{total area}}$$

target area of
a single molecule
$\sigma = \pi d^2$
σ : *microscopic collision cross section of one molecule*

Total target area
$\sigma_{\text{tot}} = n\sigma L^2 \Delta x$
($n \equiv$ density)
$n\sigma$: *macroscopic collision cross section*

Total area is L^2
$\Rightarrow \quad \frac{\Delta N}{N} = n\sigma\Delta x$

Mean free path

Each of ΔN collisions scatters molecule out of the beam
$\Rightarrow$ ΔN can be interpreted as decrease in the number N

$$\Delta N = -n\sigma\Delta x \Rightarrow \frac{\Delta N}{N} = -n\sigma\Delta x$$

For very large N $\quad \frac{\Delta N}{\Delta x} \rightarrow \frac{dN}{dx}$

$\Rightarrow$ *survival equation :* $\frac{dN}{dx} = -n\sigma N \Rightarrow N = N_0 e^{-n\sigma x}$

Mean free path $(l) \equiv$ the average distance traveled by a group of N_0 molecules before they make their first collision

$$l = \frac{\sum x\Delta N_x}{N_0} = n\sigma\int_0^\infty x e^{-n\sigma x}\, dx = \frac{1}{n\sigma} \Rightarrow l = \frac{1}{n\sigma}$$

Mean free path does not depend on speed of molecules

$$\text{Example}: \ d \simeq 2 \times 10^{-10}\text{m}^2, \ n \simeq 3 \times 10^{25}\text{m}^{-3}$$

$$\Rightarrow \quad n\sigma \ = \ n\pi d^2 \ \simeq \ 4 \times 10^6\text{m}^{-1}$$

$$\Rightarrow \quad \text{mean free path} \ \ l \ = \ \frac{1}{n\sigma} \ \simeq \ 2.5 \times 10^{-7}\text{m}$$

$$\text{Average intermolecular separation} \ \simeq \ 3 \times 10^{-9}\text{m} \ \ll \ \text{mean free path}$$

If one takes into account motion of ``target” molecules:

$$\text{All molecules have the same speed} \ \Rightarrow \ l \ = \ \frac{3}{4}\frac{1}{n\sigma} \quad \text{(Clausius)}$$

$$\text{Maxwell velocity distribution} \ \Rightarrow \ l \ = \ \frac{1}{\sqrt{2}}\frac{1}{n\sigma}$$

Collision frequency *z*

$$\text{In time } \Delta t \text{ the molecule travels } \bar{v}\Delta t \text{ along the zigzag path}$$

$$\Rightarrow \ \text{average number of collisions} \ = \frac{\bar{v}\Delta t}{l} \quad \Rightarrow \quad \text{frequency } z = \frac{\bar{v}}{l}$$

$$\text{Mean free time } \tau \ \equiv \ \frac{1}{z} \ = \ \frac{1}{n\sigma\bar{v}}$$

Example :

for oxygen at room temperature

$$z \ \simeq \ 5.5 \times 10^9 \, \frac{\text{collisions}}{\text{s}}$$

$$\tau \ = \ \frac{1}{z} \ \simeq \ 1.8 \times 10^{-10}\text{s}$$

Motion of electrons in a conductor

Electrons are much smaller than ions

$\Rightarrow$ center – to – center distance is $\frac{d}{2}$ rather than d

$\Rightarrow$ electronic mean free path is $l_e = \frac{4}{n\sigma}$

where n = density and σ = cross section of *ions*

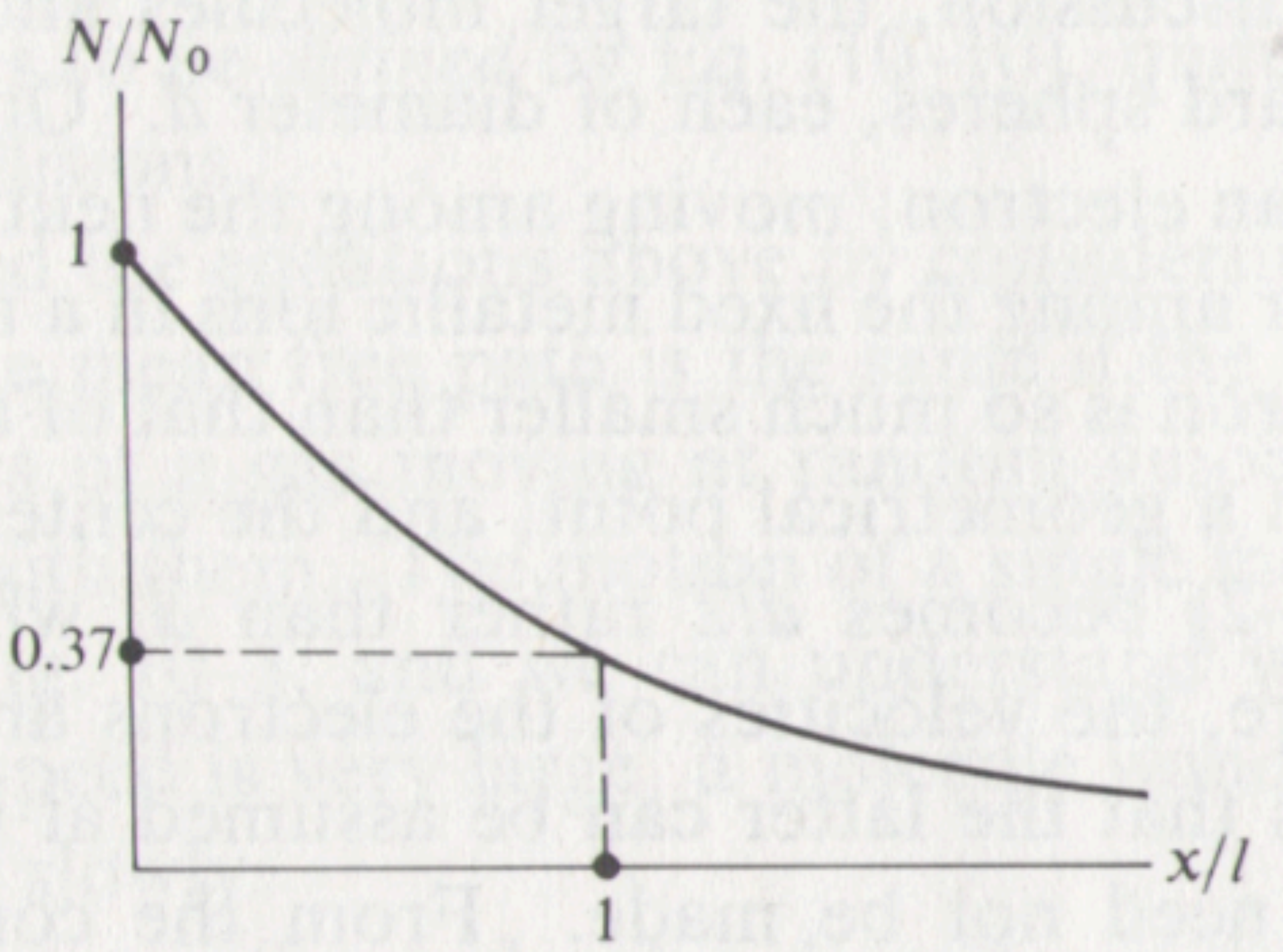
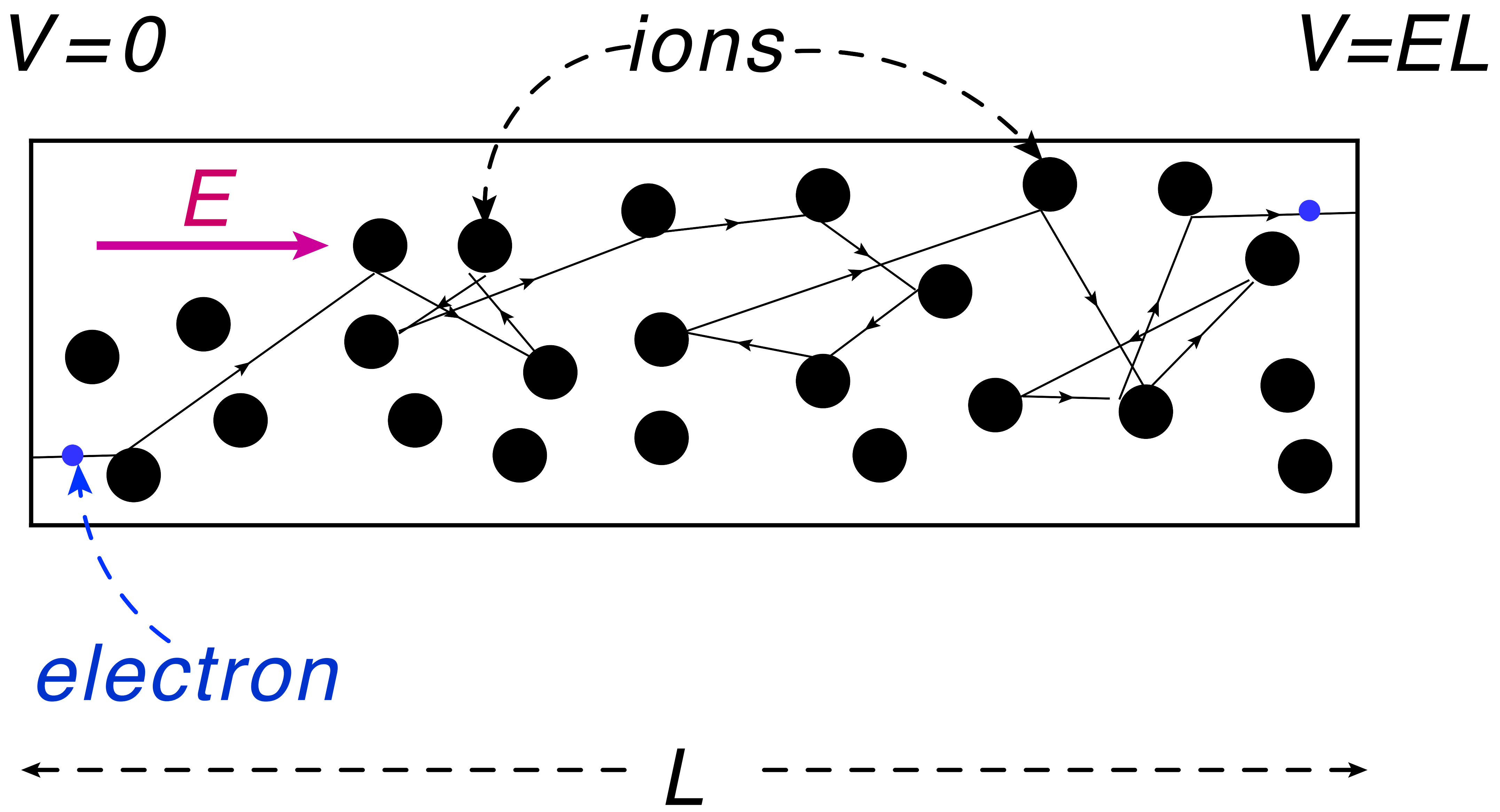


Fig. 10–5 Graph of the survival equation.

The survival equation in terms of mean free path

$$N = N_0 e^{-n\sigma x}$$
$$= N_0 e^{-x/l}$$

Ohm’s law



The acceleration $a = \frac{F}{m} = \frac{eE}{m}$

$\Rightarrow$ average *drift* velocity between collisions $u = \frac{a\tau}{2} = \frac{1}{2}\frac{eE}{m}\frac{l_e}{\bar{v}}$

Drift velocity is much smaller than average thermal speed

The current density $J \equiv$ the current per unit of cross sectional area

The current density J (current per unit of cross sectional area is a product of of the number density n_e of electrons, their charge e and drift velocity u

$$J = n_e e u = \frac{n_e e^2 l_e}{2mv} E$$

Since $I = JA$ and $V = EL$ we get Ohm′s law

$$I = \frac{n_e e^2 l_e}{2mvL} VA \Leftrightarrow I = \frac{V}{R}, \quad R = \frac{2mvL}{n_e e^2 l_e A}$$

Gas viscosity

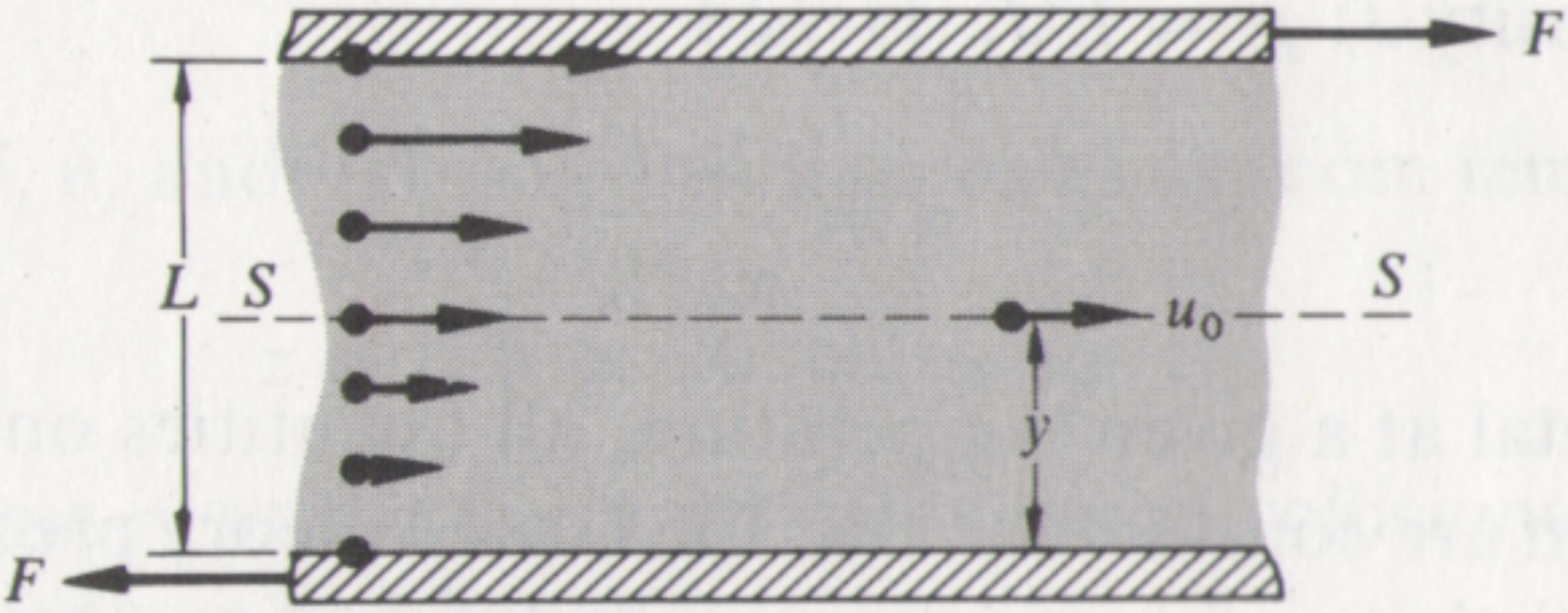


Fig. 10–6 Viscous flow between a stationary lower plate and a moving upper plate.

The molecules in the layer of the gas have a forward velocity component *u* which increases uniformly with the distance *y* above the lower plate

The *coefficient of viscosity* of the gas η is defined by $$\frac{F}{A} = \eta\frac{du}{dy}$$

$$\frac{du}{dy} \equiv \text{the } \textit{velocity gradient}$$

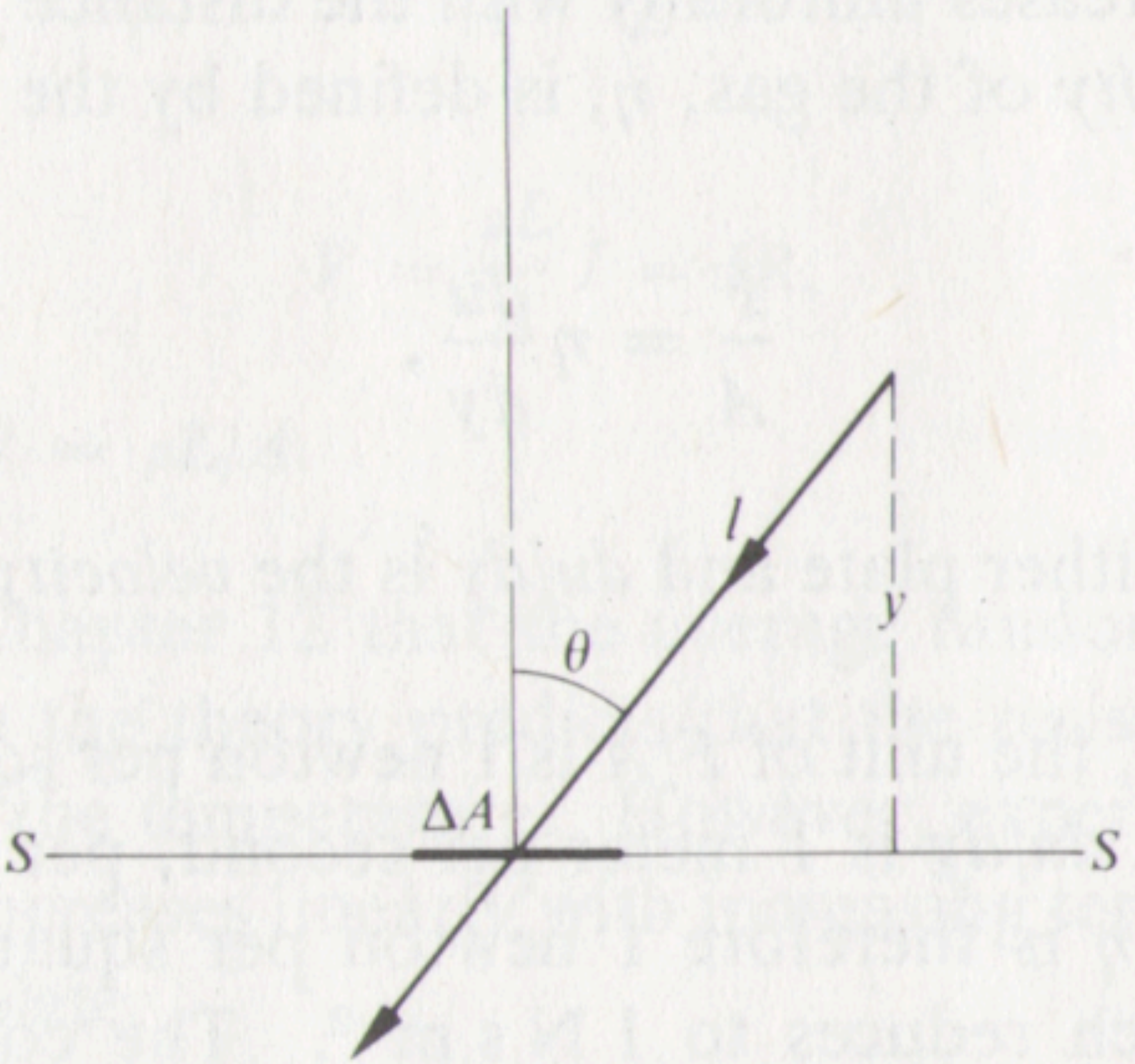


Fig. 10–7 The last mean free path before the molecule crosses the surface started a distance $y = l\cos\theta$ from the surface.

To find the net momentum $\bar{G}\downarrow$ in the direction of the flow carried across the surface (per unit time and per unit area) we need to find the average height $\bar{y}$ at which a molecule made its last collision before crossing

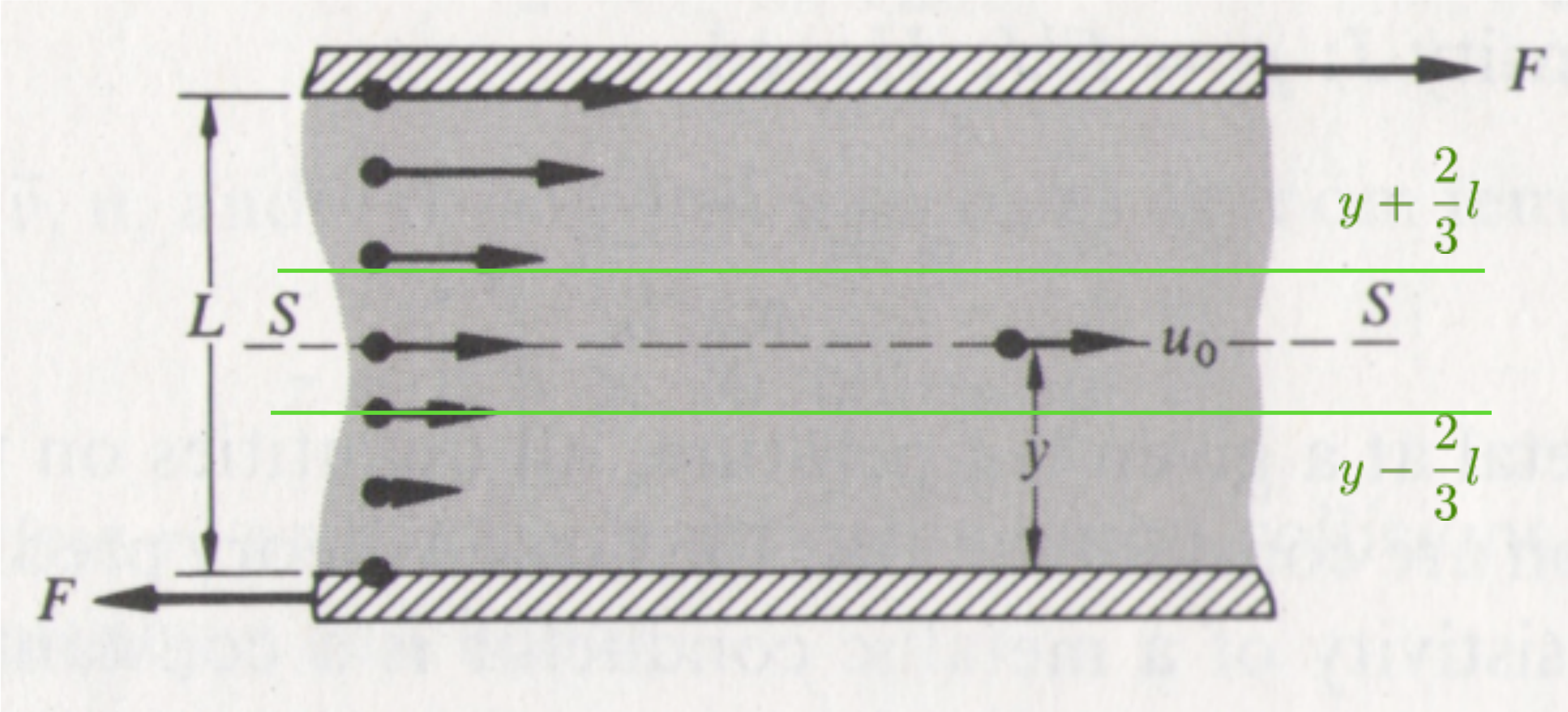
The average $\bar{y}$ is found by multiplying $l\cos\theta$ by the flux $\Delta\Phi_\theta$, summing over all θ and diving by the total flux Φ

$$\Delta\Phi_{\theta v} \;=\; \tfrac{v}{2}\Delta n_v \sin\theta\cos\theta\Delta\theta \quad\Rightarrow$$

$$\Delta\Phi_{\theta} \;=\; \tfrac{1}{2}\sum v\Delta n_v \sin\theta\cos\theta\Delta\theta \;=\; \tfrac{\bar{v}}{2} n \sin\theta\cos\theta\Delta\theta$$

$$\Phi \;=\; \tfrac{1}{4}\bar{v}n \quad\Rightarrow\quad \frac{\Delta\Phi_\theta}{\Phi} \;=\; 2\sin\theta\cos\theta\Delta\theta \quad\Rightarrow$$

$$\bar{y} \;=\; \sum l\cos\theta\frac{\Delta\Phi_\theta}{\Phi} \;\rightarrow\; 2l\int_0^{\pi/2} d\theta\;\sin\theta\cos^2\theta \;=\; \tfrac{2}{3}l \quad\Rightarrow\quad \bar{y} \;=\; \tfrac{2}{3}l$$



$$u \;=\; u_0 + \frac{2}{3}l\frac{du}{dy}$$

$$u \;=\; u_0 - \frac{2}{3}l\frac{du}{dy}$$

Fig. 10–6 Viscous flow between a stationary lower plate and a moving upper plate.

The momentum in the direction of the flow carried across the surface per unit time and per unit area

$$\bar{G}\downarrow \;=\; m\left(u_0 + \frac{2}{3}l\frac{du}{dy}\right) \times (\text{total flux } \Phi) \;=\; \frac{1}{4}nm\bar{v}\left(u_0 + \frac{2}{3}l\frac{du}{dy}\right)$$

Similarly,

$$\bar{G}\uparrow \;=\; \frac{1}{4}nm\bar{v}\left(u_0 - \frac{2}{3}l\frac{du}{dy}\right)$$

$\Rightarrow$ the net rate of transport of momentum per unit area is

$$\bar{G} \;=\; \bar{G}\downarrow - \bar{G}\uparrow \;=\; \frac{1}{3}nm\bar{v}l\frac{du}{dy}$$

By Newton′s 2nd law $\bar{G}$ is a viscous force per unit area so

$$\eta \;=\; \frac{F}{A}\Big/\frac{du}{dy} \;=\; \frac{1}{3}nm\bar{v}l \;=\; \frac{m\bar{v}}{3\sigma}$$

$$\Rightarrow \;\eta \;=\; \frac{m\bar{v}}{3\sigma}$$

Note that η depends only on T

From statistical thermodynamics $\bar{v} \;=\; \sqrt{\frac{8kT}{\pi m}}$

$$\Rightarrow \;\eta \;=\; \frac{1}{3}\sqrt{\frac{8k}{\pi}}\,\frac{\sqrt{mT}}{\sigma}$$

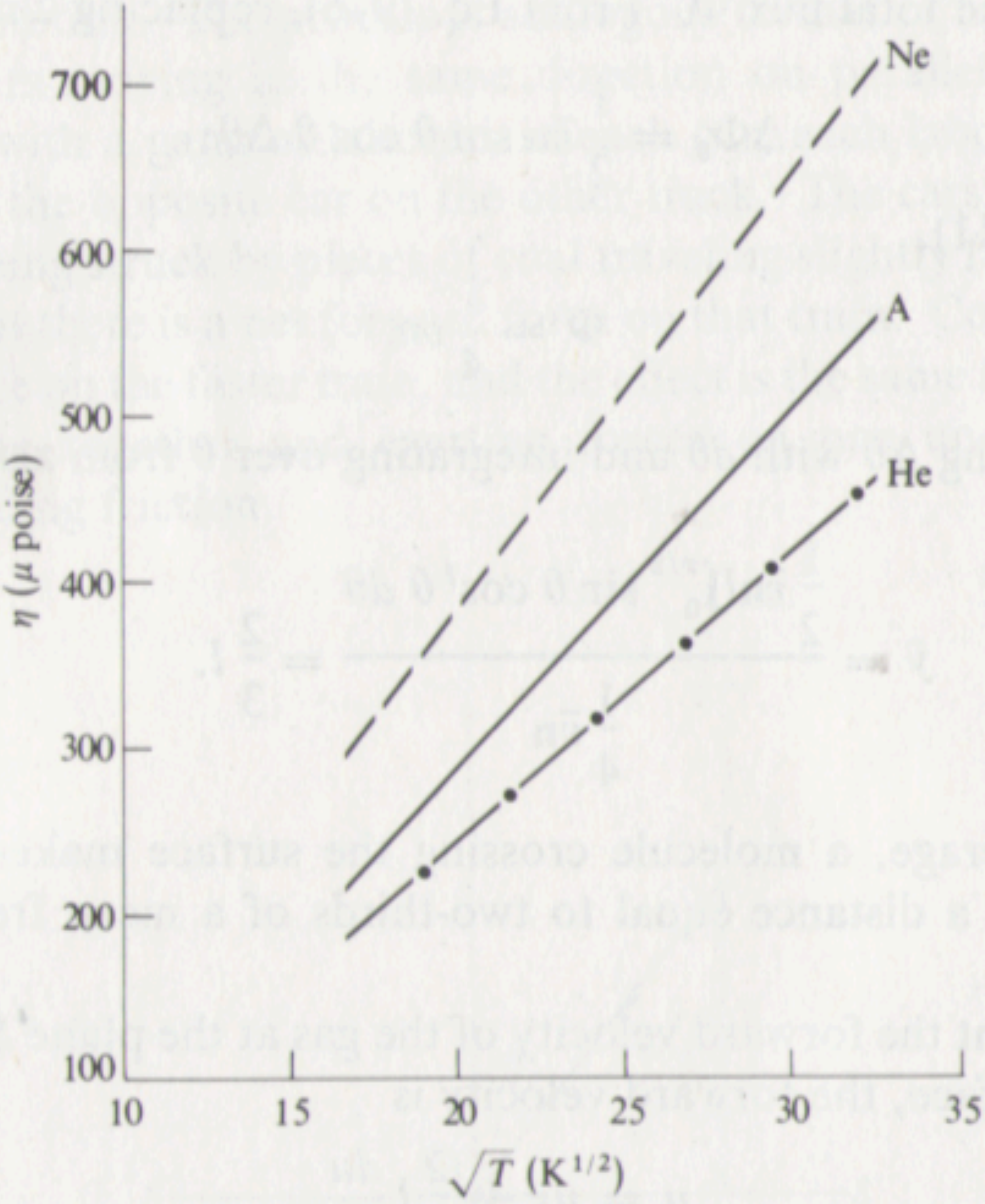


Fig. 10–8 The viscosity of helium, argon, and neon is almost a linear function of $\sqrt{T}$.

From statistical thermodynamics :

$$\eta \;=\; \frac{1}{3}\sqrt{\frac{8k}{\pi}}\,\frac{\sqrt{mT}}{\sigma}$$

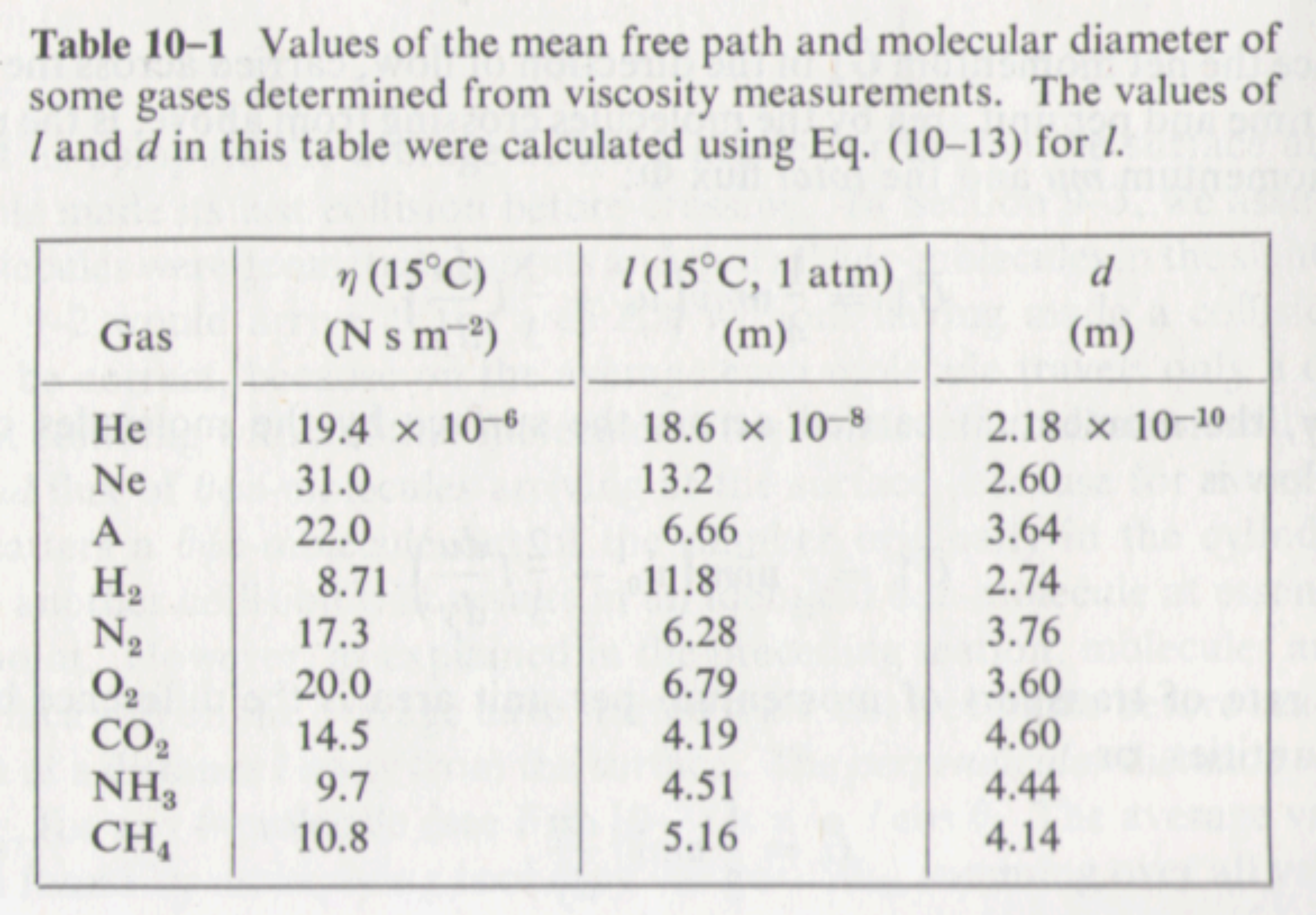
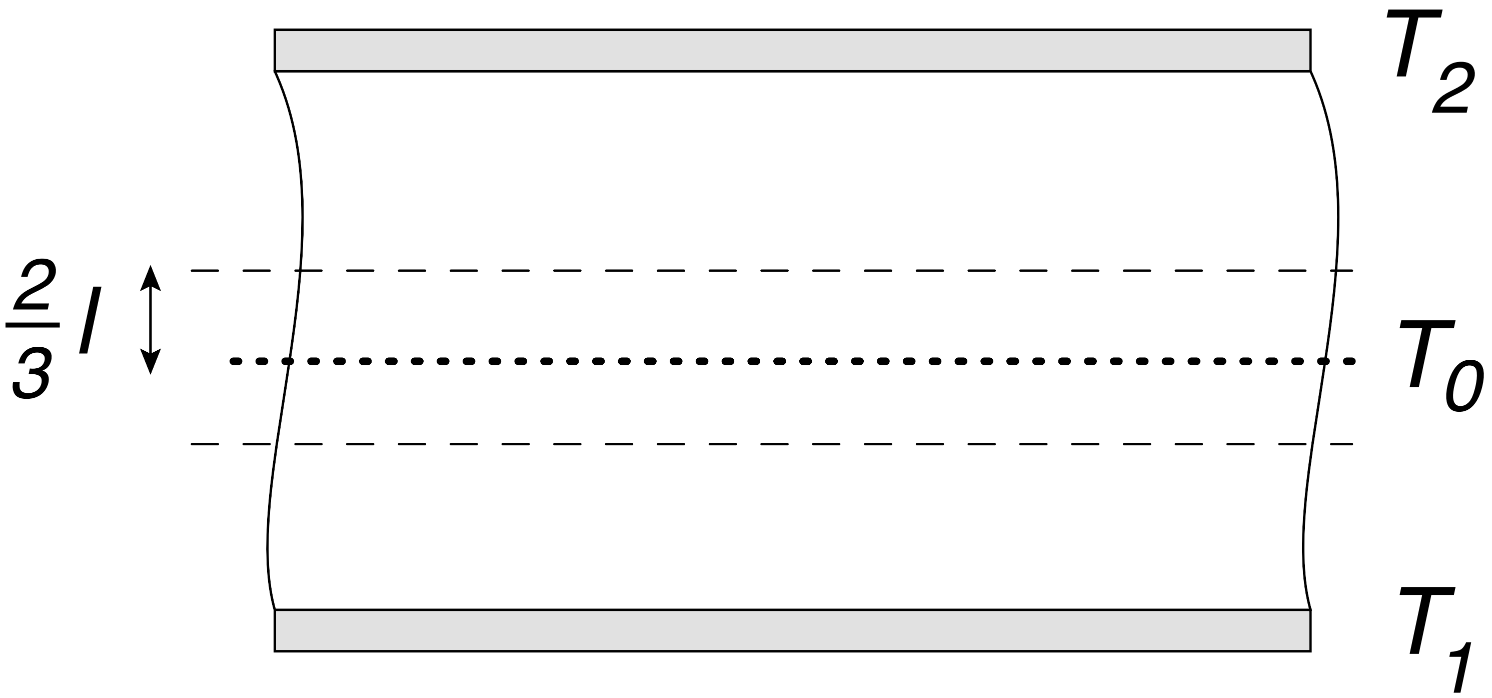


Table 10–1 Values of the mean free path and molecular diameter of some gases determined from viscosity measurements. The values of l and d in this table were calculated using Eq. (10–13) for l.

Gas	η (15°C) ($\mathrm{N\,s\,m^{-2}}$)	l (15°C, 1 atm) (m)	d (m)
He	19.4×10^{-6}	18.6×10^{-8}	2.18×10^{-10}
Ne	31.0	13.2	2.60
A	22.0	6.66	3.64
H_2	8.71	11.8	2.74
N_2	17.3	6.28	3.76
O_2	20.0	6.79	3.60
CO_2	14.5	4.19	4.60
NH_3	9.7	4.51	4.44
CH_4	10.8	5.16	4.14

From statistical thermodynamics : $\eta = \frac{1}{3}\sqrt{\frac{8k}{\pi}}\,\frac{\sqrt{mT}}{\sigma}$

Thermal conductivity λ



Heat flow per unit area per unit time $H = -\lambda \frac{dT}{dy}$

Average kinetic energy per molecule at a distance $\frac{2l}{3}$ above the surface is $c_v^* T = c_v^*(T_0 + \frac{2}{3}l\frac{dT}{dy})$

$\Rightarrow$ the energy transported downward is

$c_v^*(T_0 + \frac{2}{3}l\frac{dT}{dy}) \times$ flux $\Rightarrow H\!\downarrow = \frac{n\bar{v}}{4}c_v^*(T_0 + \frac{2}{3}l\frac{dT}{dy})$

Similarly, the energy transposted upward is $H\!\uparrow = \dfrac{n\bar{v}}{4}c_v^*(T_0 - \dfrac{2}{3}l\dfrac{dT}{dy})$

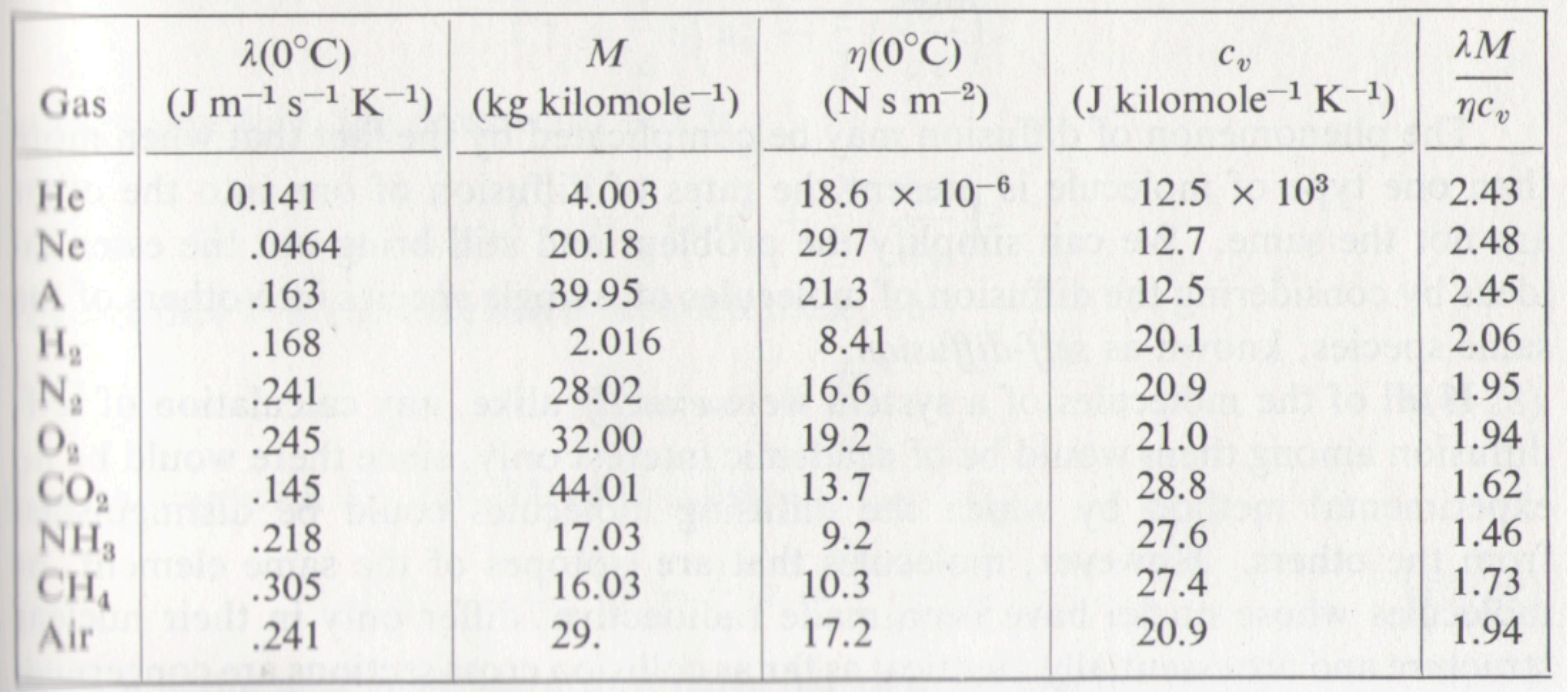
the net rate of transport per unit area is $H = H\!\uparrow - H\!\downarrow = -\dfrac{1}{3}n\bar{v}c_v^* l\dfrac{dT}{dy}$

$\Rightarrow$ the thermal conductivity is $\lambda = \frac{1}{3}n\bar{v}c_v^* l = \frac{\bar{v}c_v^*}{3\sigma}$

The ratio of thermal conductivity to viscosity is (M = atomic weight)

$$\frac{\lambda}{\eta} = \frac{c_v^*}{m} = \frac{c_v}{mN_A} = \frac{c_v}{M} \quad \Leftrightarrow \quad \frac{\lambda M}{\eta c_v} = 1$$

For real gases



Gas	$\lambda(0^\circ\mathrm{C})$ $(\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}})$	M $(\mathrm{kg\,kilomole^{-1}})$	$\eta(0^\circ\mathrm{C})$ $(\mathrm{N\,s\,m^{-2}})$	c_v $(\mathrm{J\,kilomole^{-1}\,K^{-1}})$	$\frac{\lambda M}{\eta c_v}$
He	0.141	4.003	18.6×10^{-6}	12.5×10^{3}	2.43
Ne	.0464	20.18	29.7	12.7	2.48
A	.163	39.95	21.3	12.5	2.45
H_2	.168	2.016	8.41	20.1	2.06
N_2	.241	28.02	16.6	20.9	1.95
O_2	.245	32.00	19.2	21.0	1.94
CO_2	.145	44.01	13.7	28.8	1.62
NH_3	.218	17.03	9.2	27.6	1.46
CH_4	.305	16.03	10.3	27.4	1.73
Air	.241	29.	17.2	20.9	1.94

Diffusion

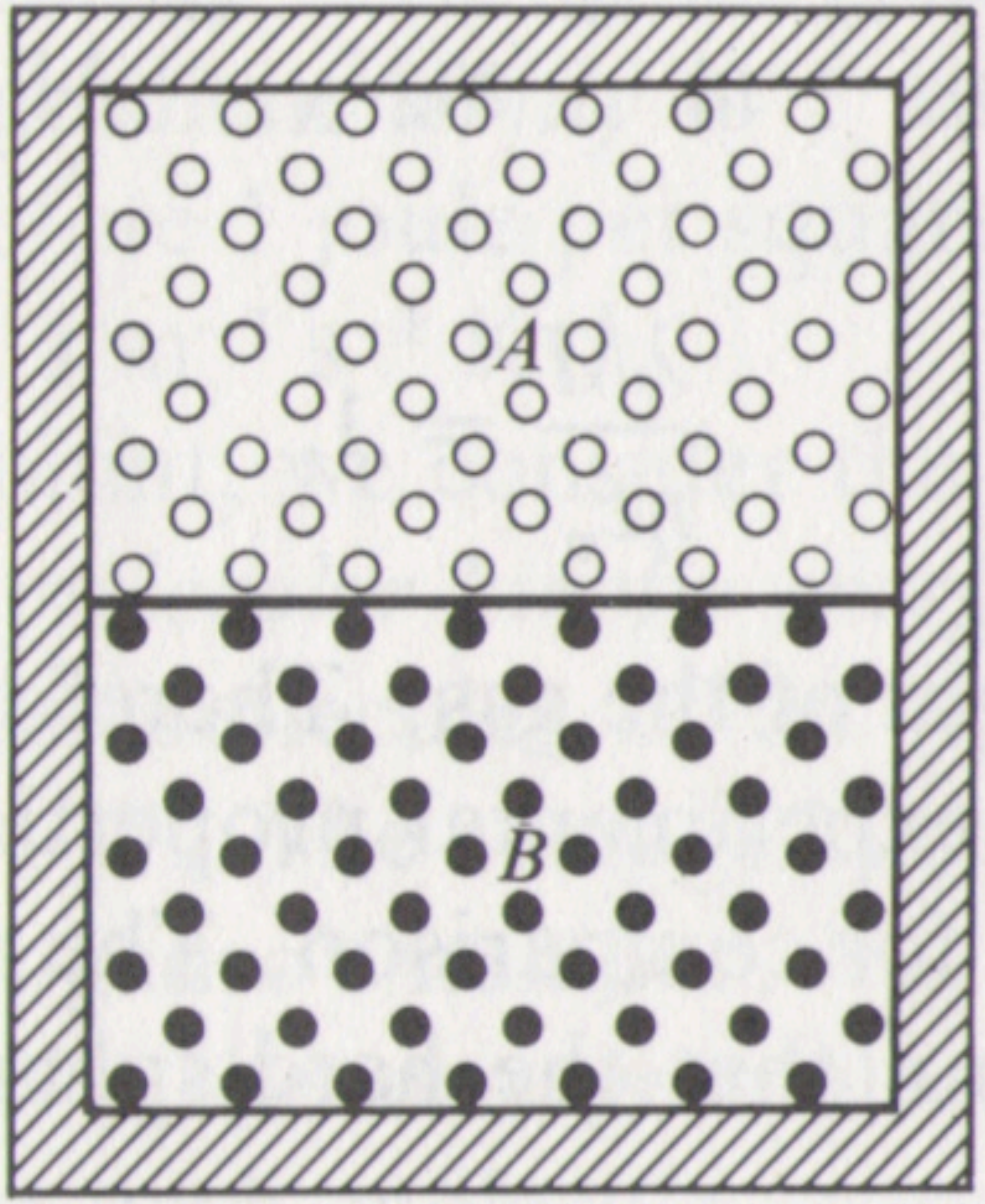


Fig. 10–9 A vessel containing two different gases separated by a partition.

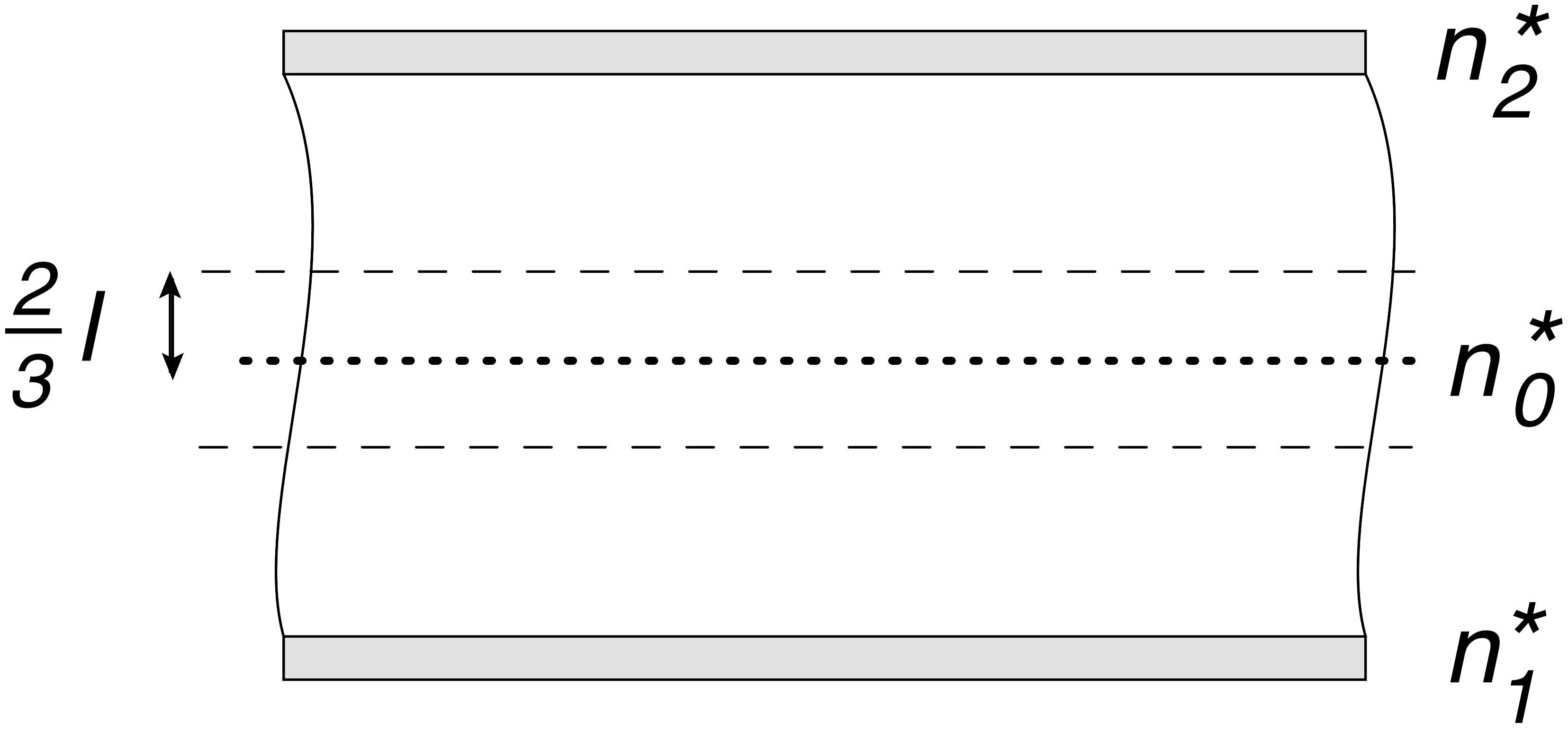
For simplicity, consider self-diffusion: two gases are the same, but one of them somehow tagged (e.g. radioactive isotope)

$$n^*(y) \equiv \text{number density of tagged molecules} \quad .$$

The flux of tagged molecules is

$$\Gamma = -D\frac{dn^*}{dy}$$

$$D \equiv \text{coefficient of self} - \text{diffusion}$$



Again, we assume that each molecule makes its last collision before crossing at a perpendicular distance (2/3)l from the surface.

$$\text{Above the surface } n^* = n_0^* + \frac{2}{3l}\frac{dn^*}{dy}$$

$$\Rightarrow \text{the downward flux is } \Gamma\downarrow = \frac{\bar{v}}{4}\left(n_0^* + \frac{2}{3}l\frac{dn^*}{dy}\right)$$

$$\text{Similarly, the upward flux is } \Gamma\uparrow = \frac{\bar{v}}{4}n^*(y) = \frac{\bar{v}}{4}\left(n_0^* - \frac{2}{3}l\frac{dn^*}{dy}\right)$$

$$\Rightarrow \text{ the coefficient of diffusion is } D = \frac{1}{3}\bar{v}l = \frac{\bar{v}}{3n\sigma}$$

where n is a *total* number of molecules per unit volume

Summary

$$\bar{G} = \left(\tfrac{1}{3} n \bar{v} l\right) \frac{d(mu)}{dy}, \qquad mu \equiv \text{flow momentum of a molecule}$$

$$H = -\left(\tfrac{1}{3} n \bar{v} l\right) \frac{d c_v^* T}{dy}, \qquad c_v^* T \equiv \text{kinetic energy of a molecule}$$

$$\Gamma = -\left(\tfrac{1}{3} n \bar{v} l\right) \frac{d \frac{n^*}{n}}{dy}, \qquad \frac{n^*}{n} \equiv \text{concentration of tagged molecules}$$

$$\eta = \tfrac{1}{3} n m \bar{v} l = \frac{\bar{v} m}{3\sigma} \qquad \leftarrow \text{coefficient of viscosity}$$

$$\lambda = -\tfrac{1}{3} n c_v^* \bar{v} l = \frac{\bar{v} c_v^*}{3\sigma} \qquad \leftarrow \text{coefficient of thermal conductivity}$$

$$D = -\tfrac{1}{3} n \bar{v} l = \frac{\bar{v}}{3 n \sigma} \qquad \leftarrow \text{coefficient of self} - \text{diffusion}$$

From quantum mechanics

In non – relativistic quantum mechanics a particle is described by complex *wave function* $\Psi(t,\vec{r})$ satisfying *Schrodinger equation*

$$i\hbar\frac{\partial\Psi(t,\vec{r})}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(t,\vec{r}) + \mathcal{V}(t,\vec{r})\Psi(t,\vec{r})$$

$\mathcal{V}(t,\vec{r}) =$ potential energy

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \Leftrightarrow \quad \nabla^2\Psi(t,\vec{r}) = \frac{\partial^2\Psi(t,\vec{r})}{\partial x^2} + \frac{\partial^2\Psi(t,\vec{r})}{\partial y^2} + \frac{\partial^2\Psi(t,\vec{r})}{\partial z^2}$$

$$\hbar = \frac{h}{2\pi} = 1.0545718\times 10^{-34}\frac{\mathrm{m^2 kg}}{\mathrm{sec}}$$

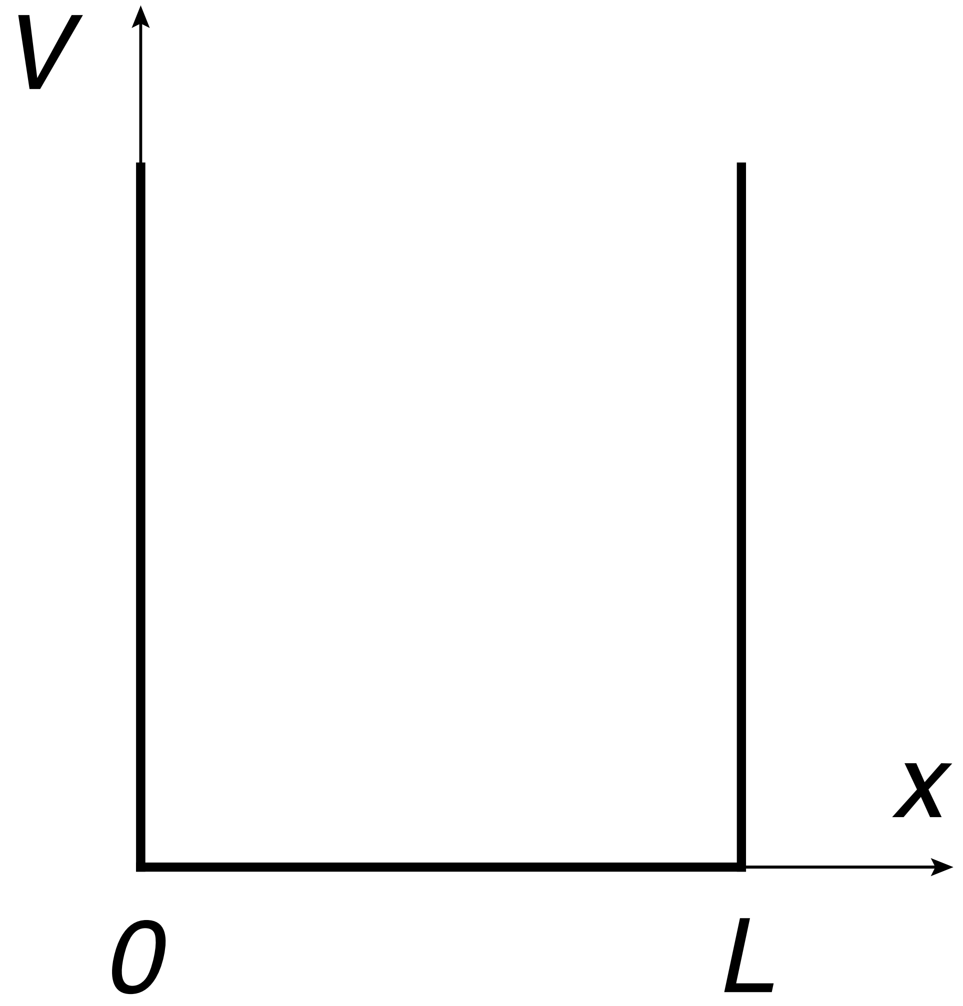
$|\Psi(t,\vec{r}|^2\Delta V \quad = \quad$ *probability*

to find the particle in the volume $\Delta V = \Delta x\Delta y\Delta z$

Stationary state with energy E : $\quad \Psi(t,\vec{r}) = e^{-\frac{i}{\hbar}Et}\Psi(\vec{r})$

$\Rightarrow \quad -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r}) + \mathcal{V}(x)\Psi(\vec{r}) = E\Psi(\vec{r})$ stationary Schrodinger equation

Particle in a box in one dimension



$$1 - \text{dim Schrodinger equation}:$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2} + \mathcal{V}(x)\Psi(x) = E\Psi(x)$$

For a particle in the box

$$\left.\begin{aligned} \mathcal{V}(x) &= 0 \quad \text{if } 0 < x < L, \\ \mathcal{V} &= \infty \quad \text{otherwise} \end{aligned}\right\} \Rightarrow$$

$$\Rightarrow \left\{ \begin{aligned} \frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2} &= E\Psi(x) \\ \Psi(0) = \Psi(L) &= 0 \end{aligned}\right.$$

Mathematically, it is the equation describing standing waves

$$\text{Solution}: \quad \Psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{\pi n x}{L}, \qquad \int_0^L |\Psi_n(x)|^2 dx = 1$$

$$E_n = \frac{\pi^2 n^2 \hbar^2}{2mL^2} \quad \leftarrow \quad \underline{\textit{energy levels}} \qquad n = \text{integer number}$$

=> Energy is *quantized*

Classical analog: standing waves

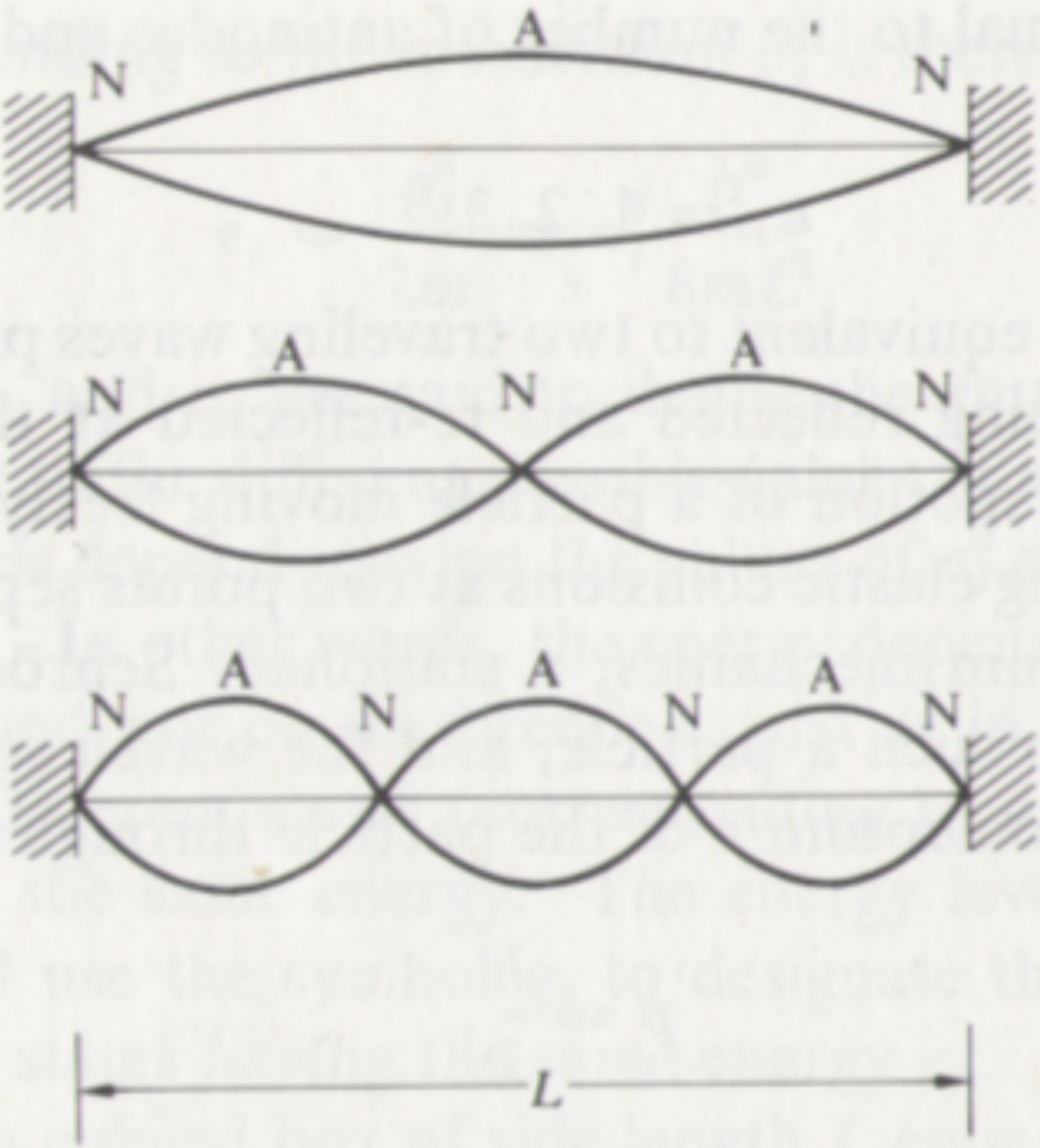


Fig. 11–1 Three of the possible stationary waves in a stretched string fixed at both ends.

$$n = 1: \quad \sin\frac{\pi x}{L}$$

$$n = 2: \quad \sin\frac{2\pi x}{L}$$

$$n = 3: \quad \sin\frac{3\pi x}{L}$$

A standing wave is a superposition of left-moving and right-moving waves

$$\Psi_n(t,x) \;=\; \frac{1}{2i}\left(e^{-i\frac{E_n}{\hbar}t+i\frac{p_n}{\hbar}x} - e^{-i\frac{E_n}{\hbar}t-i\frac{p_n}{\hbar}x}\right)$$

$$p_n \;=\; \frac{\pi n}{L} \quad - \quad \text{quantized momenta,} \qquad E_n \;=\; \frac{p_n^2}{2m}$$

Particle in a box in three dimensions

$$\mathcal{V}(\vec{r}) \;=\; 0 \;\; \text{if} \;\; L > x, y, z > 0, \qquad \mathcal{V} = \infty \text{ otherwise}$$

$$\Psi_{\vec{n}}(t,\vec{r}) \;=\; \left(\tfrac{2}{L}\right)^{\frac{3}{2}} \sin\frac{\pi n_x x}{L} \sin\frac{\pi n_y y}{L} \sin\frac{\pi n_z z}{L}$$

$$\vec{n} \;\equiv\; (n_x, n_y, n_z)$$

$$\vec{p}_{\vec{n}} \;=\; \left(\frac{\pi n_x}{L}, \frac{\pi n_y}{L}, \frac{\pi n_z}{L}\right), \qquad E_{\vec{n}} \;=\; \frac{\vec{p}^{\,2}_{\vec{n}}}{2m} \;=\; \frac{\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Energy levels are *degenerate*, e.g. $E_{1,2,3} \;=\; E_{1,3,2}$ etc.

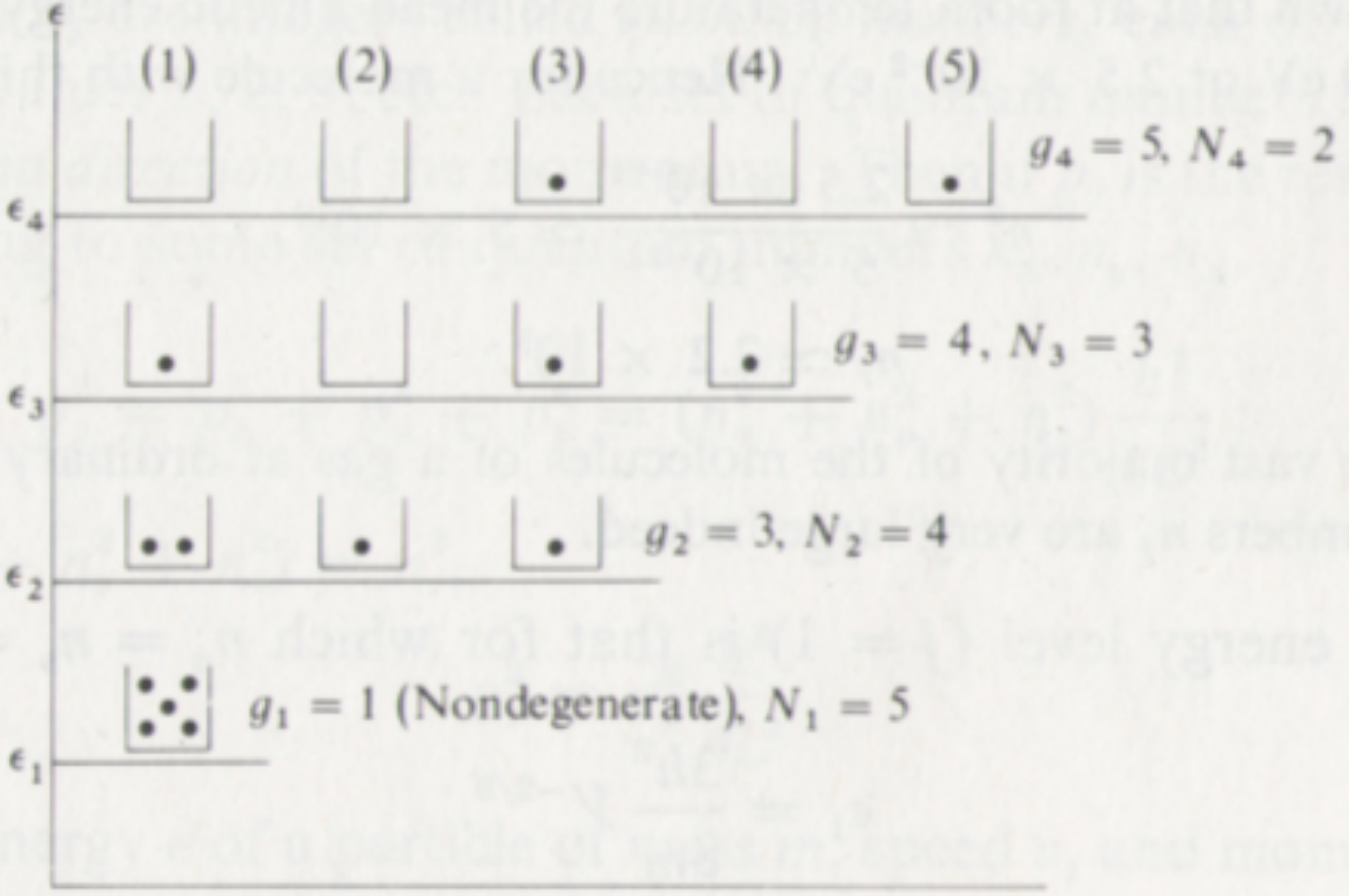


Fig. 11–2 A schematic representation of a set of energy levels ϵ_j, their degeneracies g_j and their occupation numbers N_j.

$g_j \equiv$ degeneracy

$N_j \equiv$ occupation number

$$\sum N_j = N$$

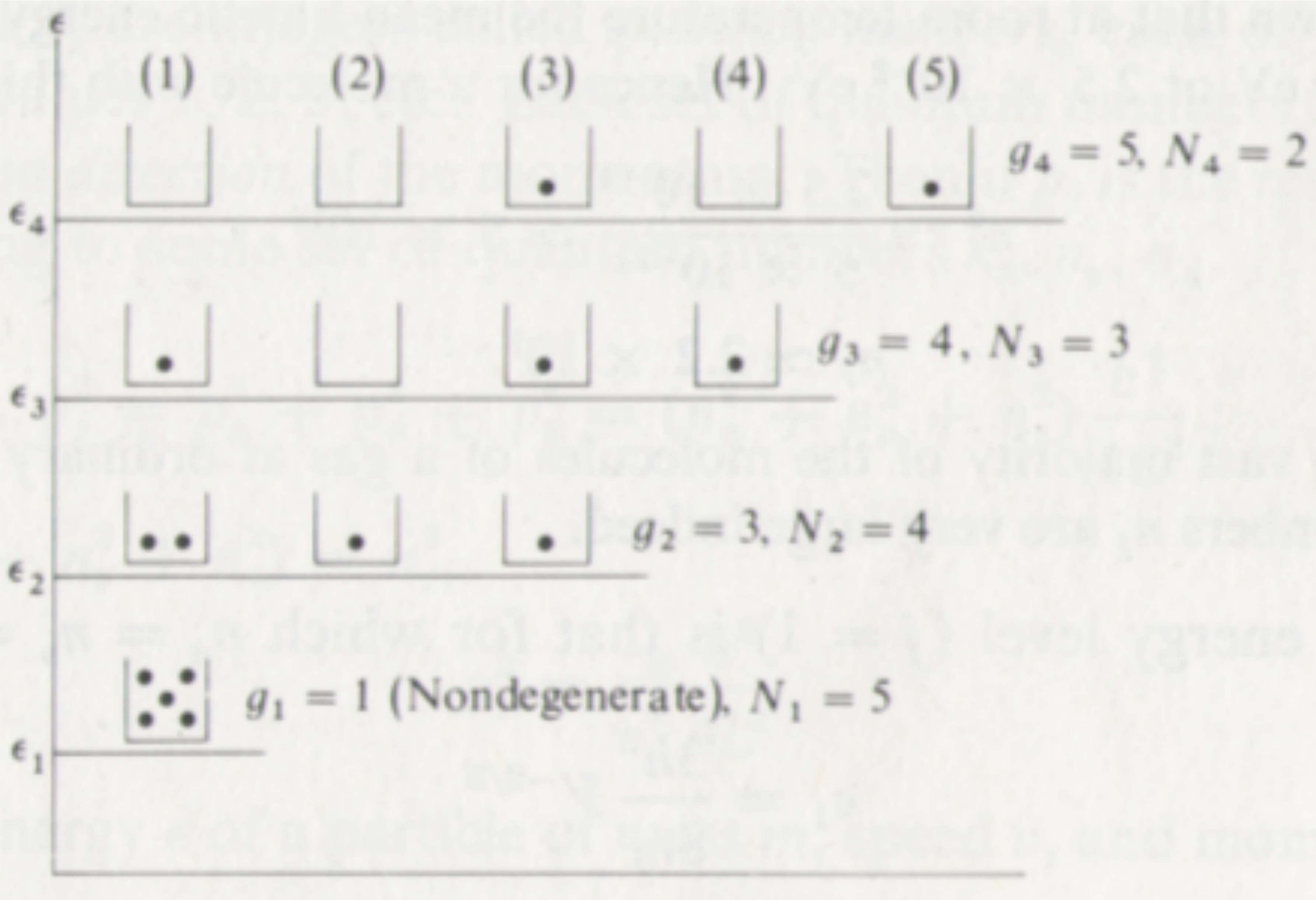
$$\sum \epsilon_j N_j = E$$

$$E = \frac{\pi^2 \hbar^2}{2mL^2}\left(5 + 4 \times 2^2 + 3 \times 3^2 + 2 \times 4^2\right)$$

Statistical Thermodynamics

Macrostates and microstates

Macrostate of this *assembly: (5,4,3,2)*



Microstate of the assembly for indistinguishable particles :

5 particles in state $(1)_1$;
two particles in state$(1)_2$
and one particle in each
of $(2)_2$ and $(3)_2$;
one particle in each of
states $(1)_3$, $(3)_3$, and $(4)_3$;
one particle in each of
states $(3)_4$ and $(5)_4$

For distinguishable particles, to describe the microstate one has to specify particle of which sort is in each state.

Thermodynamic probability

Postulate of statistical thermodynamics:

All possible microstates of an isolated assembly are equally probable

Two ways to interpret:

1. Take $t \to \infty$ and call Δt the time which system is in one of its microstates, then Δt is the same for all microstates.

2. Take $\mathcal{N} \to \infty$ replicas of a given assembly. At any time, let $\Delta\mathcal{N}$ be the number of replicas in which the system is in a given microstate, then $\Delta\mathcal{N}$ is the same for all microstates.

The number of equally probable microstates that correspond to a given macrostate k is called the *thermodynamic probability* $\mathcal{W}_k$ of a macrostate k

Thermodynamic probability of the assembly $\Omega \equiv \sum_k \mathcal{W}_k$

The goal of statistical theory is to find the *occupation number* $\bar{N}_j$ of level j $\equiv$

$\equiv$ average number of particles at the level j

Let N_{jk} be the occupation number of level j in the macrostate k then the *group average* value of the occupation number of level j is

$$\bar{N}_j^g \;=\; \tfrac{1}{\mathcal{N}} \textstyle\sum_k N_{jk} \mathcal{W}_k \Delta\mathcal{N} \;=\; \frac{\sum_k N_{jk} \mathcal{W}_k \Delta\mathcal{N}}{\sum_k \mathcal{W}_k \Delta\mathcal{N}} \;=\; \tfrac{1}{\Omega} \textstyle\sum_k N_{jk} \mathcal{W}_k$$

$\mathcal{N} \;=\;$ total number of replicas, $\Delta\mathcal{N} \;\equiv\;$ number of replicas in a macrostate

Next, let us find

$\bar{N}_g^t \;\equiv\;$ the *time average* of the occupation number of level j

$$\bar{N}_j^t \;=\; \tfrac{1}{t} \textstyle\sum_k N_{jk} \mathcal{W}_k \Delta t \;=\; \frac{\sum_k N_{jk} \mathcal{W}_k \Delta t}{\sum_k \mathcal{W}_k \Delta t} \;=\; \tfrac{1}{\Omega} \textstyle\sum_k N_{jk} \mathcal{W}_k$$

$t \to \infty$, $\Delta t \;\equiv\;$ the time which system spends in a macrostate

$$\Rightarrow \quad \bar{N}_j^g \;=\; \bar{N}_j^t \;\equiv\; \bar{N}_j$$

The formula for $\bar{N}_j$ depends on the type of statistics (Bose – Einstein, Fermi – Dirac, or Maxwell – Boltzmann)

Bose-Einstein statistics

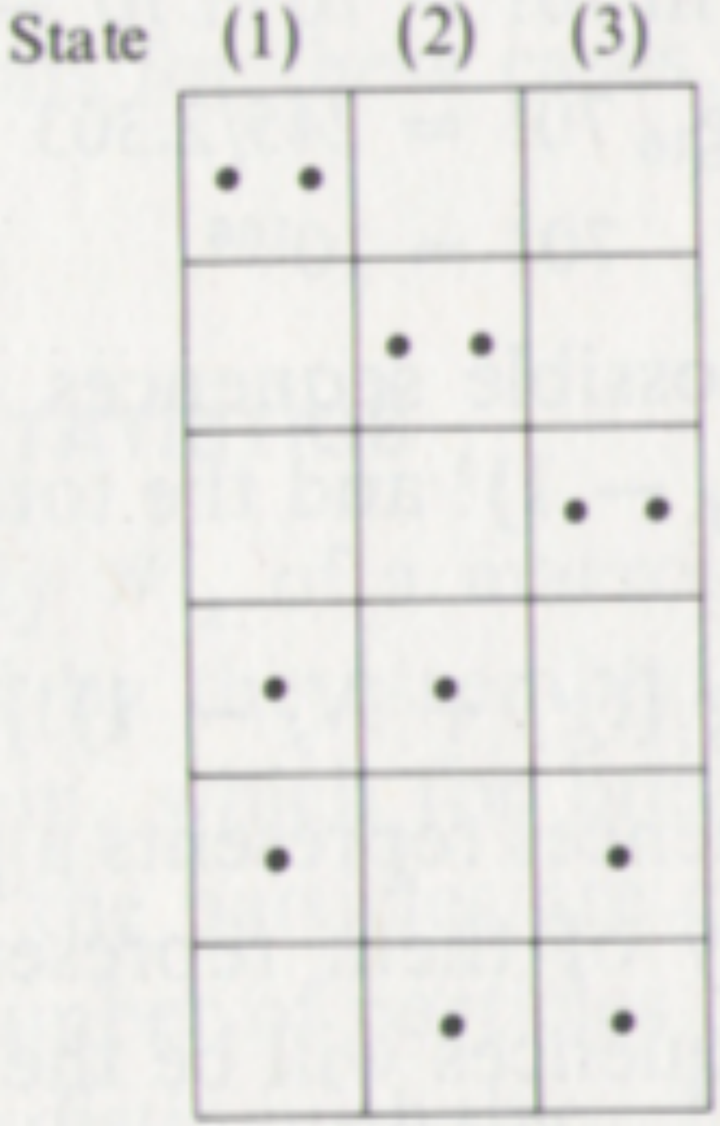
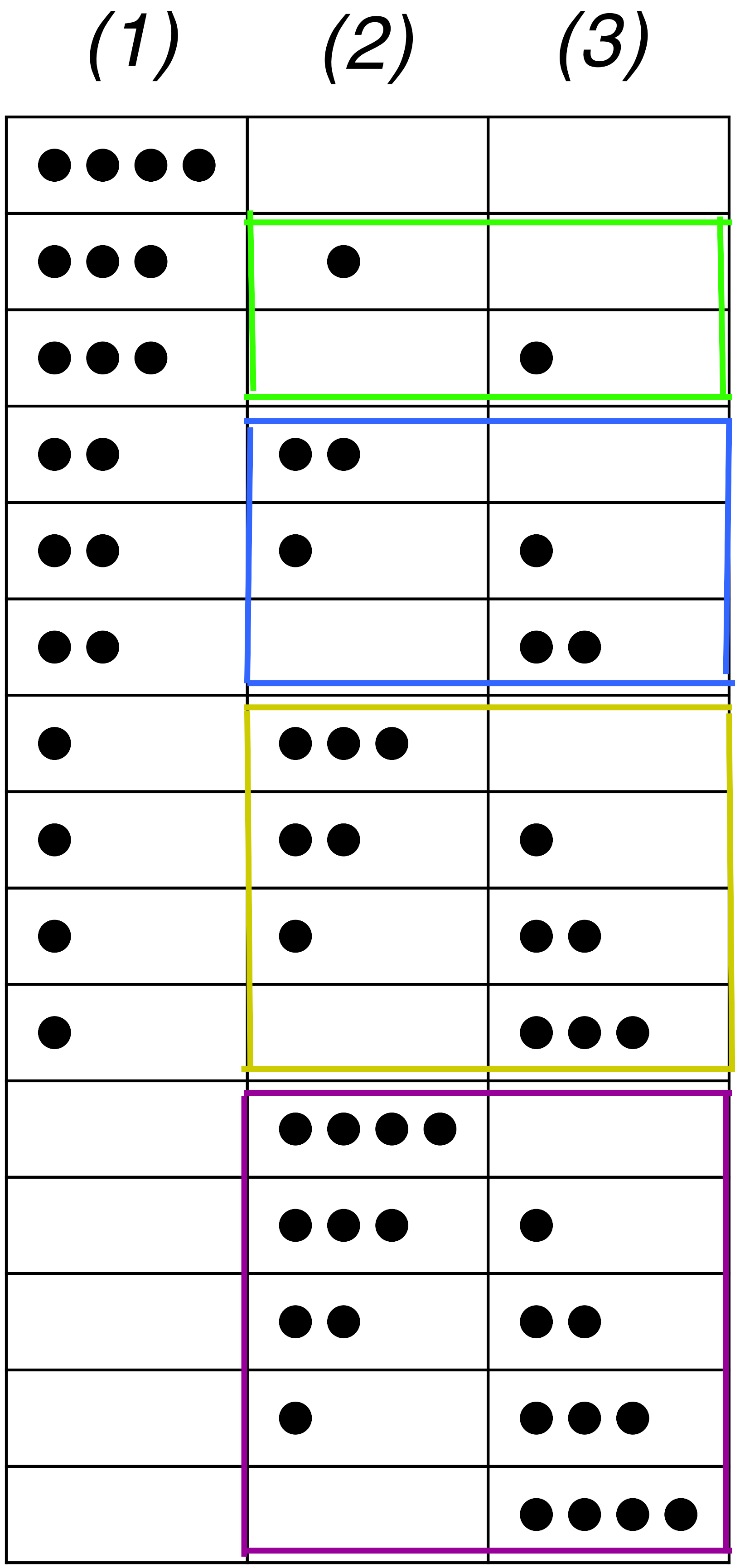


Fig. 11–3 The possible distributions of two indistinguishable particles among three energy states, with no restriction on the number of particles in each state.

$\omega(g_j, N_j) \;\equiv\;$ the number of different distributions of N_j indistinguishable particles between g_j degeneratete states

For $g_j = 3$ and $N_j = 2$
$\omega(g_j, N_j) = \omega(3, 2) = 6$



(1)	(2)	(3)
●●●●		
●●●	●	
●●●		●
●●	●●	
●●	●	●
●●		●●
●	●●●	
●	●●	●
●	●	●●
●		●●●
	●●●●	
	●●●	●
	●●	●●
	●	●●●
		●●●●

For $g = 3$ and $N = 4$

$$\omega(3,4) = 1 + \omega(2,1) + \omega(2,2) + \omega(2,3) + \omega(2,4)$$

In general

$$\omega(g,N) = 1 + \omega(g-1,1) + \omega(g-1,2) + \omega(g-1,3) + \omega(g-1,4) + \ldots + \omega(g-1,N)$$

Solution of this *recursive relation*

$$\omega(g,N) = \frac{(g+N-1)!}{(g-1)!N!}$$

convention : $0! = 1$

The number of microstates of N_j particles at level j is

$$\omega(g_j, N_j) = \frac{(g_j+N_j-1)!}{(g_j-1)!N_j!}$$

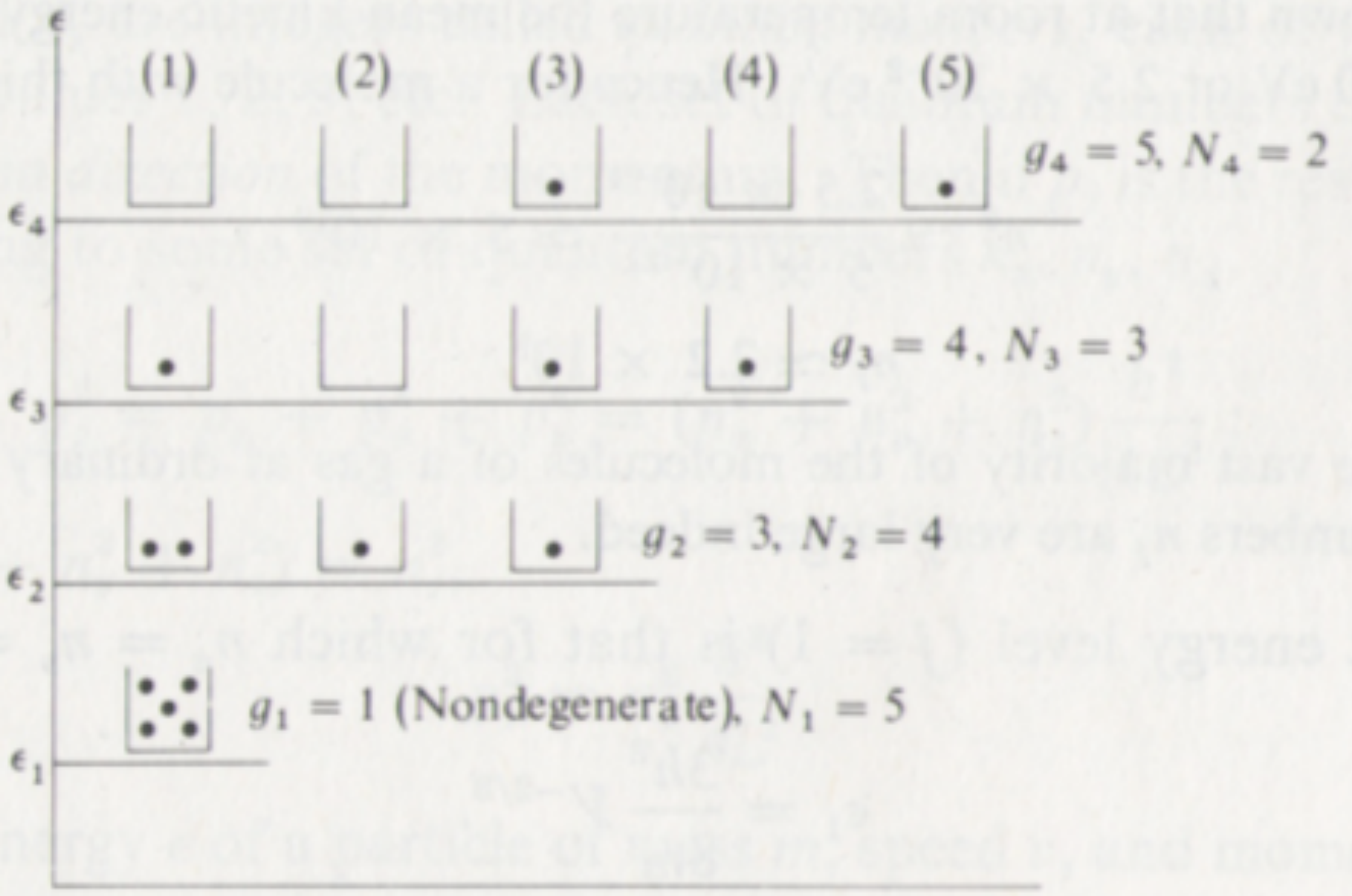


Fig. 11–2 A schematic representation of a set of energy levels ϵ_j, their degeneracies g_j and their occupation numbers N_j.

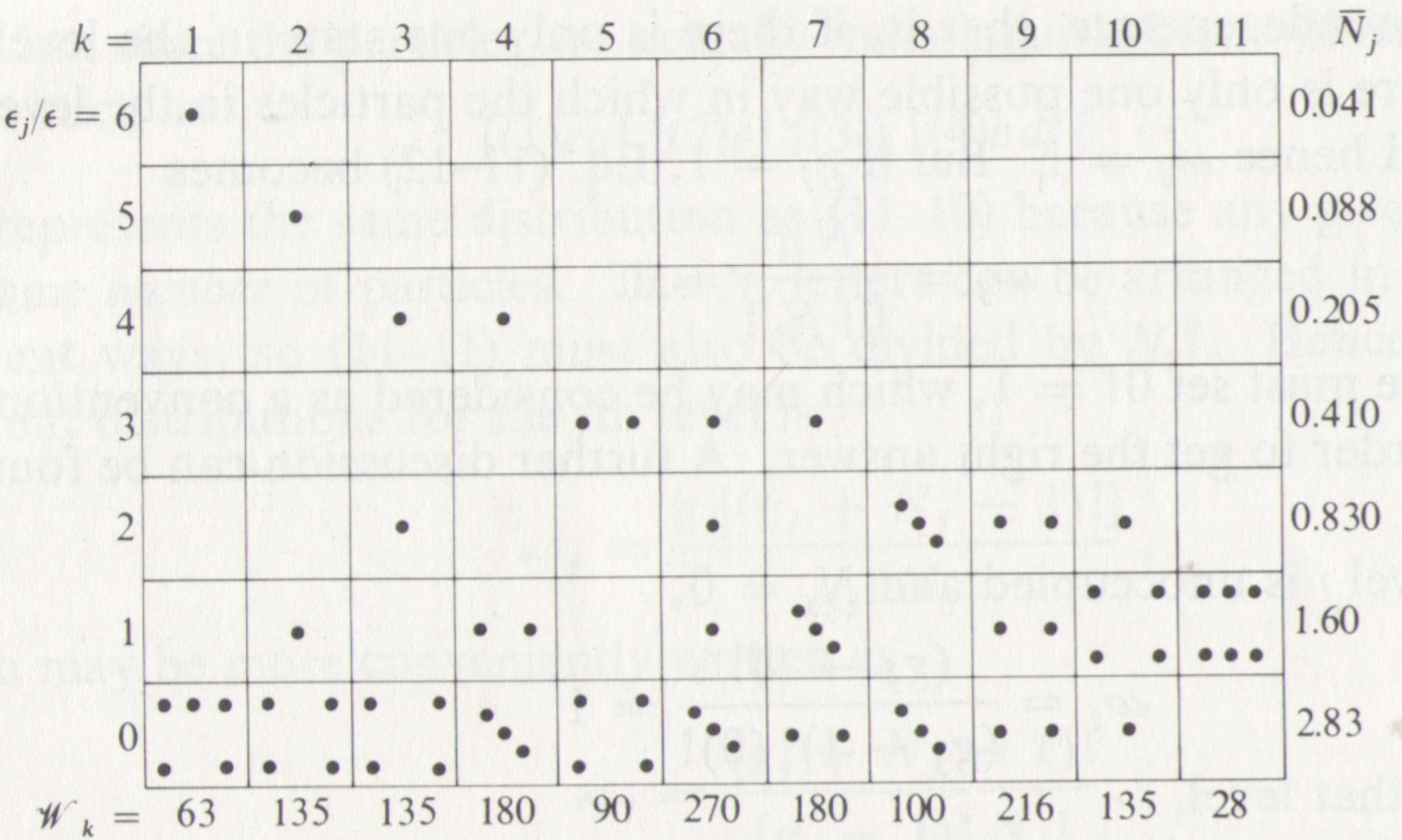
For example, the number of microstates in a macrostate $(5, 4, 3, 2)$ is

$$\omega(1,5)\omega(3,4)\omega(4,3)\omega(5,2)$$

In general, the number of microstates in a macrostate $k = (N_1, N_2, ..N_j...)$ is

$$\mathcal{W}_k = \prod_j \omega_j$$

$$= \prod_j \frac{(g_j+N_j-1)!}{(g_j-1)!N_j!}$$



$$\Omega = \sum_k \mathcal{W}_k$$

$$\bar{N}_j = \frac{\sum_k N_{jk} W_k}{\Omega}$$

Fig. 11–4 The eleven possible macrostates of an assembly of 6 particles obeying Bose-Einstein statistics. The energy levels are equally spaced and have a degeneracy $g_j = 3$ in each level. The total energy of the system is $U = 6\epsilon$. The thermodynamic probability of each macrostate is given at the bottom and the average occupation number of each level is printed on the right of the diagram.

$$180 = \frac{5!}{2!3!}\frac{4!}{2!2!}\frac{3!}{2!} \;\text{ etc,} \qquad 0.83 = \frac{135 + 270 + 3 \times 100 + 2 \times 216 + 135}{1532} \;\text{ etc}$$

Fermi-Dirac statistics

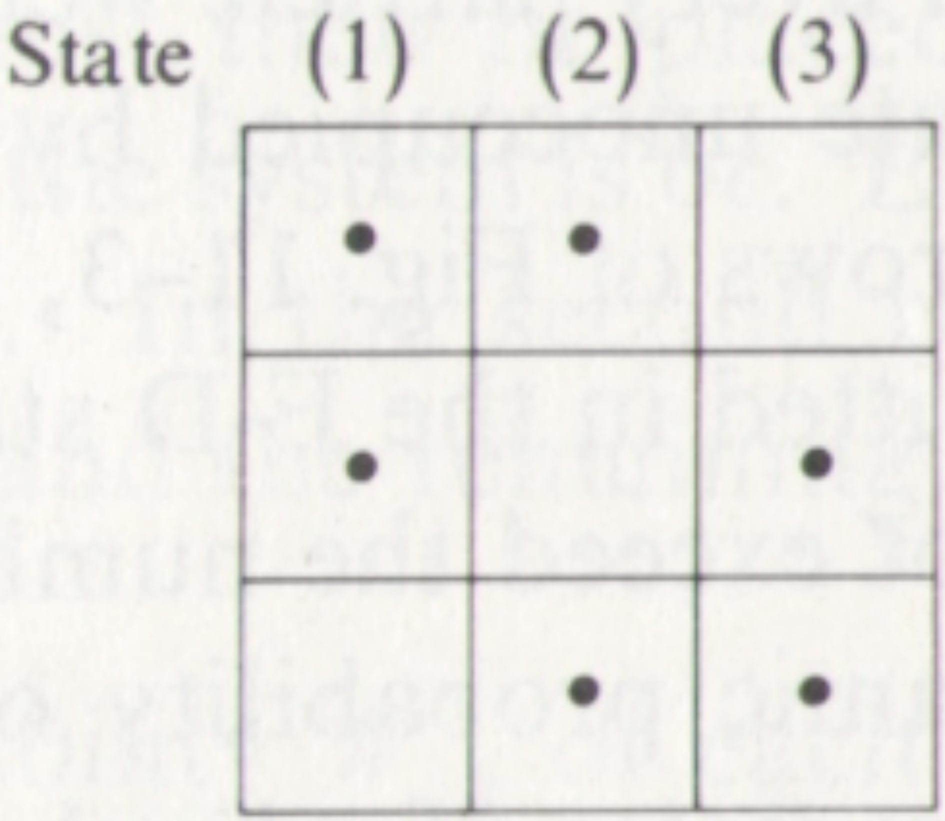
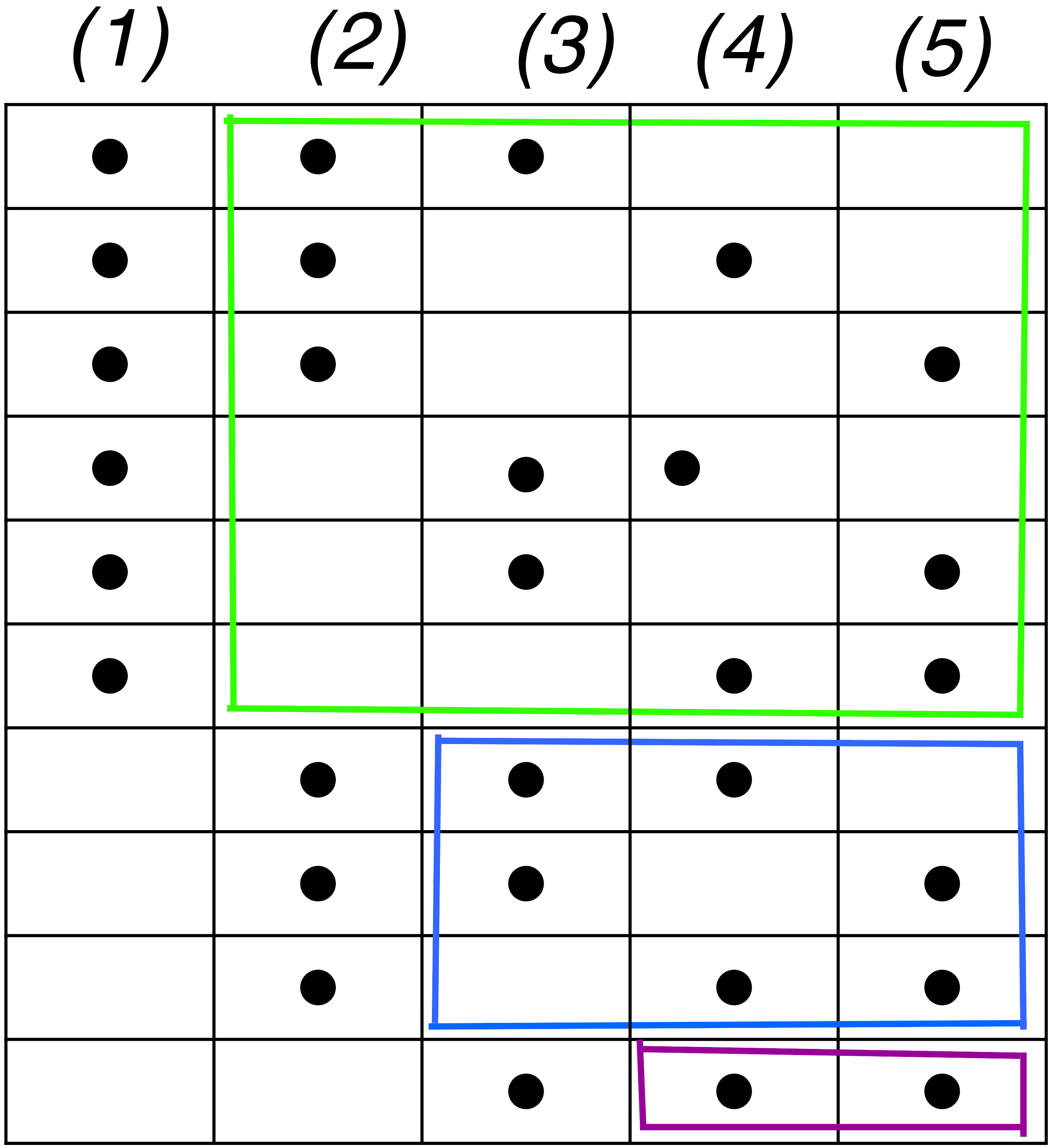


Fig. 11–5 The possible distributions of two indistinguishable particles among three energy states, with no more than one particle in each state.

For $g_j = 3$ and $N_j = 2$
$\omega(g_j, N_j) = \omega(3, 2) = 3$



For $g = 5$ and $N = 3$

$$\omega(5,3) = \omega(4,2) + \omega(3,2) + 1$$
$$= 6 + 3 + 1 = 10$$

In general

$$\omega(g,N)$$
$$= \omega(g-1, N-1)$$
$$+ \omega(g-2, N-1)$$
$$+ \omega(g-3, N-1)$$
$$+ \ldots + \omega(N-2, N-1) + 1$$

Solution of this recursive relation

$$\omega(g,N) = \frac{g!}{(g-N)!N!}$$

The number of microstates of N_j particles at level $j \geq N_j$ is $\omega(g_j, N_j) = \frac{(g_j)!}{(g_j - N_j)!N_j!}$

The number of microstates of N_j particles at level $j \geq N_j$ is $\omega(g_j, N_j) = \frac{(g_j)!}{(g_j - N_j)! N_j!}$

For example, the number of microstates in a macrostate $(1, 2, 3, 2)$ is $\omega(1,1)\omega(3,2)\omega(4,3)\omega(5,2)$

In general, the number of microstates in a macrostate is

$$\mathcal{W}_k = \prod_j \omega_j = \prod_j \frac{g_j!}{(g_j - N_j)! N_j!}$$

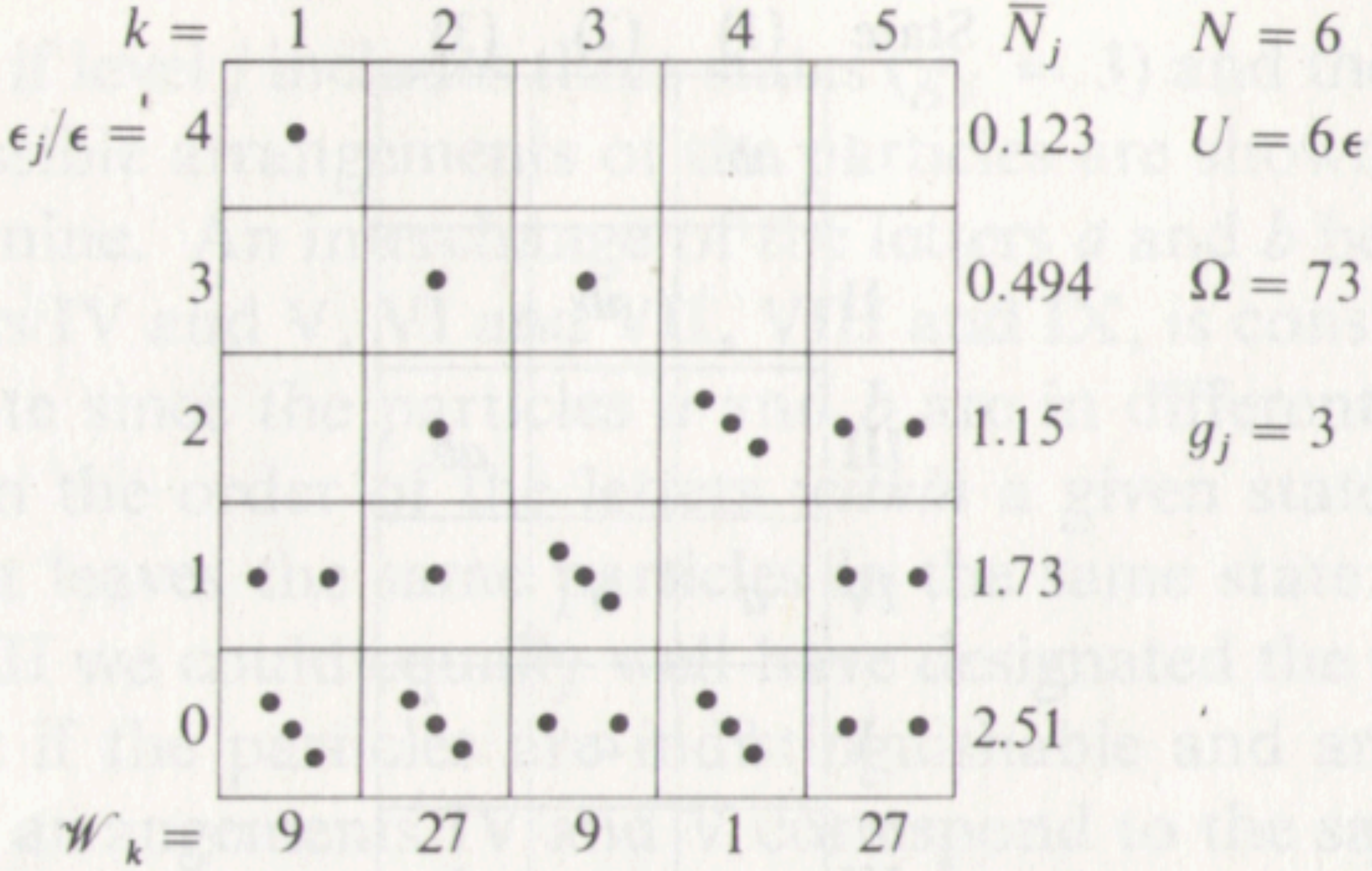


Fig. 11–6 The five possible macrostates of an assembly of 6 particles obeying Fermi-Dirac statistics. The energy levels are equally spaced and have a degeneracy of $g_j = 3$ each. The total energy of the system is $U = 6\epsilon$. The thermodynamic probability of each macrostate is given at the bottom, and the average occupation number of each level is printed on the right of the diagram.

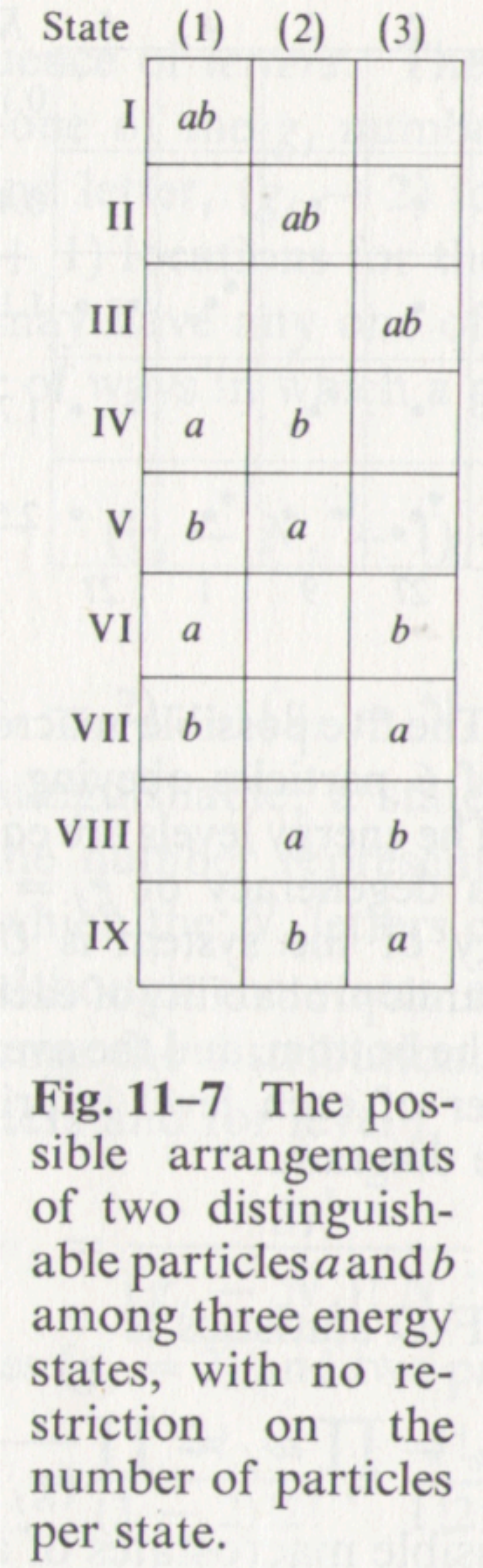
$$9 = \frac{3!}{3!}\,\frac{3!}{2!}\,\frac{3!}{2!}$$

$$27 = \frac{3!}{3!}\,\frac{3!}{2!}\,\frac{3!}{2!}\,\frac{3!}{2!}$$

$$1.15 =$$
$$= \frac{27+3+27\times 2}{73}$$

$$1.73 =$$
$$= \frac{9\times 2+27+9\times 3+27\times 2}{73}$$

Maxwell-Boltzmann statistics



State	(1)	(2)	(3)
I	*ab*		
II		*ab*	
III			*ab*
IV	*a*	*b*	
V	*b*	*a*	
VI	*a*		*b*
VII	*b*		*a*
VIII		*a*	*b*
IX		*b*	*a*

Fig. 11–7 The possible arrangements of two distinguishable particles *a* and *b* among three energy states, with no restriction on the number of particles per state.

Particle a can be placed in one of three slots, particle b can be placed in one of three slots

$$\Rightarrow \qquad \omega(3,2) \;=\; 9$$

In general, $\omega_j \;=\; g_j^{N_j}$

Due to possibility of interchange of particles between levels, or interchange between states at the same level

$$\mathcal{W} \;=\; N! \prod_j \frac{g_j^{N_j}}{N_j!}$$

Indeed, the total number of ways in which N particles can be distributed among the levels, with N_1 particles at level 1 N_2 particles at level 2 *etc.* is

$$\frac{N!}{N_1!N_2!\ldots} \;=\; \frac{N!}{\prod_j N_j!}$$

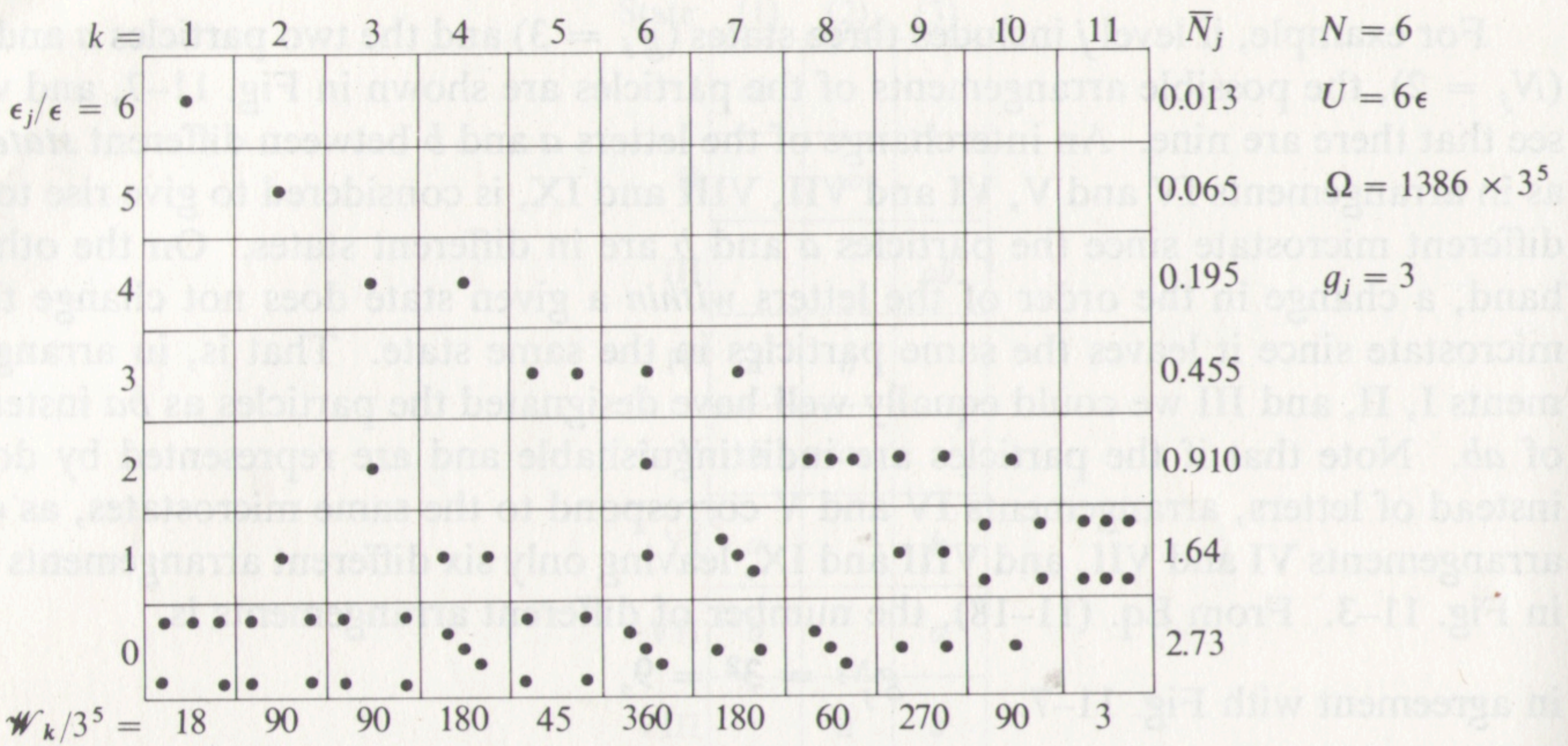


Fig. 11–8 The eleven possible macrostates of an assembly of 6 particles obeying Maxwell-Boltzmann statistics. The energy levels are equally spaced and have a degeneracy of $g_j = 3$ each. The total energy of the system is $U = 6\epsilon$. The thermodynamic probability of each macrostate is given at the bottom, and the average occupation number of each level is printed on the right of the diagram.

$$18 \times 3^5 = 6! \times \frac{3^5}{5!} \times 3, \qquad 90 \times 3^5 = 6! \times \frac{3^4}{4!} \times 3 \times 3, \quad \text{etc}$$

$$0.910 \;=\; \tfrac{1}{1386} \times \;(90 + 360 + 3 \times 60 + \;2 \times 270 + 90) \quad \text{etc.}$$

Statistical interpretation of entropy

Consider two independent systems :

$$S_{1+2} = S_1 + S_2, \qquad \Omega_{1+2} = \Omega_1 \times \Omega_2$$

$$\Rightarrow \; f(\Omega_1 \Omega_2) = f(\Omega_1) + f(\Omega_2)$$

Solution of equation $f(xy) = f(x) + f(y)$

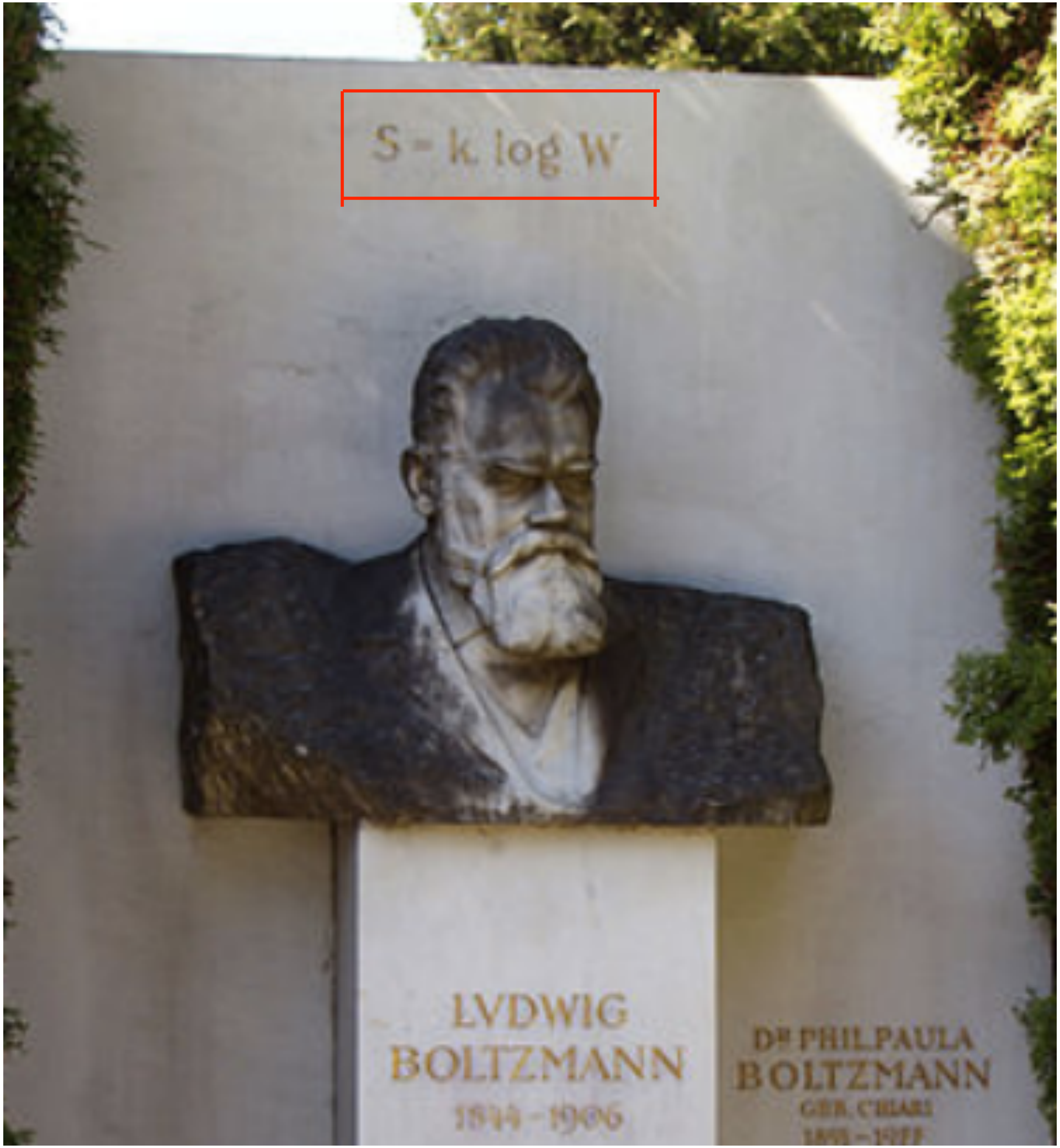
$$\frac{\partial f(xy)}{\partial x} = y \frac{df(z)}{dz}\bigg|_{z=xy},$$

$$\left.\begin{array}{l} \text{On the other hand, } \dfrac{\partial f(xy)}{\partial x} = \dfrac{df(x)}{dx} \qquad \Rightarrow \qquad \dfrac{df(x)}{dx} = y \dfrac{df(z)}{dz}\bigg|_{z=xy} \\ \text{Similarly} \\ \dfrac{\partial f(xy)}{\partial y} = x \dfrac{df(z)}{dz}\bigg|_{z=xy}, \quad \dfrac{\partial f(xy)}{\partial y} = \dfrac{df(y)}{dy} \qquad \Rightarrow \qquad \dfrac{df(y)}{dy} = x \dfrac{df(z)}{dz}\bigg|_{z=xy} \end{array}\right\} \Rightarrow$$

$$\Rightarrow \; x\frac{df(x)}{dx} = y\frac{df(y)}{dy} = \text{const} \quad \Rightarrow \quad f(x) = \text{const} \times \ln x$$

$$\Rightarrow \quad S = k \ln \Omega$$

$$\text{Later : } \; k = k_B = \frac{R}{N_A}$$


S = k. log W
LVDWIG
BOLTZMANN
1844 – 1906
Dr PHIL PAULA
BOLTZMANN
GEB. CHIARI

Bose-Einstein distribution function

Average occupation numbers for a system with large number of particles is given by *distribution function*

To find it, compare two systems :

1. System "1" with number of particles N and energy U and
2. System "2" with number of particles $N' = N - n$ and energy $U' = U - n\epsilon_r$

System "2" is system "1" with n particles removed from level r with energy ϵ_r and all other levels kept intact :

$$N'_j \overset{j \neq r}{=} N_j , \qquad N'_r = N_r - n$$

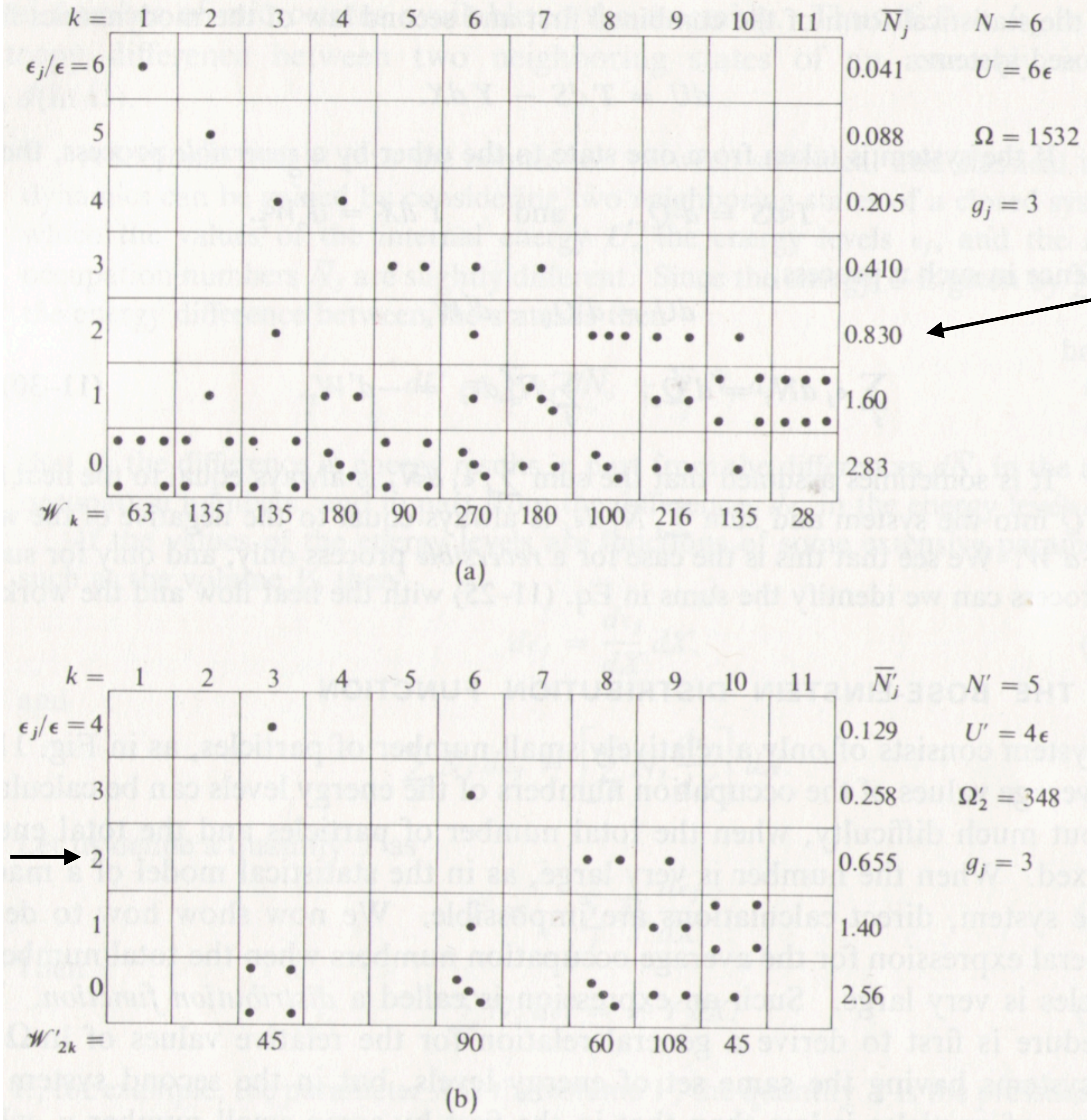


Fig. 11–9 (a) The possible macrostates of an assembly of 6 particles obeying B-E statistics when $U = 6\epsilon$. (b) The possible macrostates when one particle is removed from level 2 of the assembly of part (a). The thermodynamic probability of each macrostate is given at the bottom and the average occupation number of each level is printed on the right of the diagram.

System ``2”:
n=1 particle is
removed from
level r=2
of system ``1”

$$U' = U - 2\epsilon = 4\epsilon$$

The probability $\mathcal{W}_k$ of a macrostate k in system "1" is

$$\mathcal{W}_k = \prod_j \frac{(g_j + N_{jk} - 1)!}{(g_j - 1)! N_{jk}!},$$

and in system "2"

$$\mathcal{W}'_{rk} = \prod_j \frac{(g_j + N'_{jk} - 1)!}{(g_j - 1)! N'_{jk}!}$$

***r* is a label**

For consistency, we adopt

$$(-1)! = \infty \Leftrightarrow \frac{1}{(-1)!} = 0$$

$$\frac{\mathcal{W}'_{rk}}{\mathcal{W}_k} = \prod_j \frac{(g_j+N'_{jk}-1)!N_{jk}!}{(g_j+N_{jk}-1)!N'_{jk}!} = \frac{N_{rk}}{g_r+N'_{rk}} \Rightarrow N_{rk}\mathcal{W}_k = (g_r + N'_{rk})\mathcal{W}'_{rk}$$

Sum over all macrostates : $\sum_k N_{rk}\mathcal{W}_k = g_r \sum_k \mathcal{W}'_{rk} + \sum_k N'_{rk}\mathcal{W}'_{rk}$

$$\sum_k N_{rk}\mathcal{W}_k = \bar{N}_k\Omega, \quad \sum_k \mathcal{W}'_{rk} = \Omega', \quad \sum_k N'_{rk}\mathcal{W}'_{rk} = \bar{N}'_r\Omega'$$

$$\Rightarrow \frac{\bar{N}_r}{\bar{N}'_r+g_r} = \frac{\Omega'}{\Omega}$$

In macroscopic systems $N_j \gg 1$ so the removal of one particle will make a small change in $\bar{N}_r$

$$\Rightarrow \frac{\bar{N}_r}{\bar{N}_r+g_r} = \frac{\Omega'}{\Omega} \Leftrightarrow \ln\frac{\bar{N}_r}{\bar{N}_r+g_r} = \ln\frac{\Omega'}{\Omega} = \ln\Omega' - \ln\Omega$$

$$S = k_B\ln\Omega \Rightarrow \ln\frac{\bar{N}_r}{\bar{N}_r+g_r} = \frac{S'-S}{k_B} = \frac{\Delta S}{k_B}$$

$$T\Delta S = \Delta U - \mu\Delta N \Rightarrow$$

for our two states $\Delta U = -\epsilon_r, \quad \Delta N = -1 \Rightarrow \Delta S = \frac{\mu-\epsilon_r}{T}$

Since level "r$''$ was arbitrary, for any level j

$$\ln \frac{\bar{N}_j}{\bar{N}_j+g_j} = \frac{\mu-\epsilon_j}{k_B T}$$

$$\Rightarrow \quad \frac{g_j+\bar{N}_j}{\bar{N}_j} = \frac{g_j}{\bar{N}_j} + 1 = \exp \frac{\epsilon_j-\mu}{k_B T}$$

$$\Rightarrow \quad \bar{N}_j = \frac{g_j}{\exp\left(\frac{\epsilon_j-\mu}{k_B T}\right)-1}$$

Bose – Einstein distribution function

Fermi-Dirac distribution function

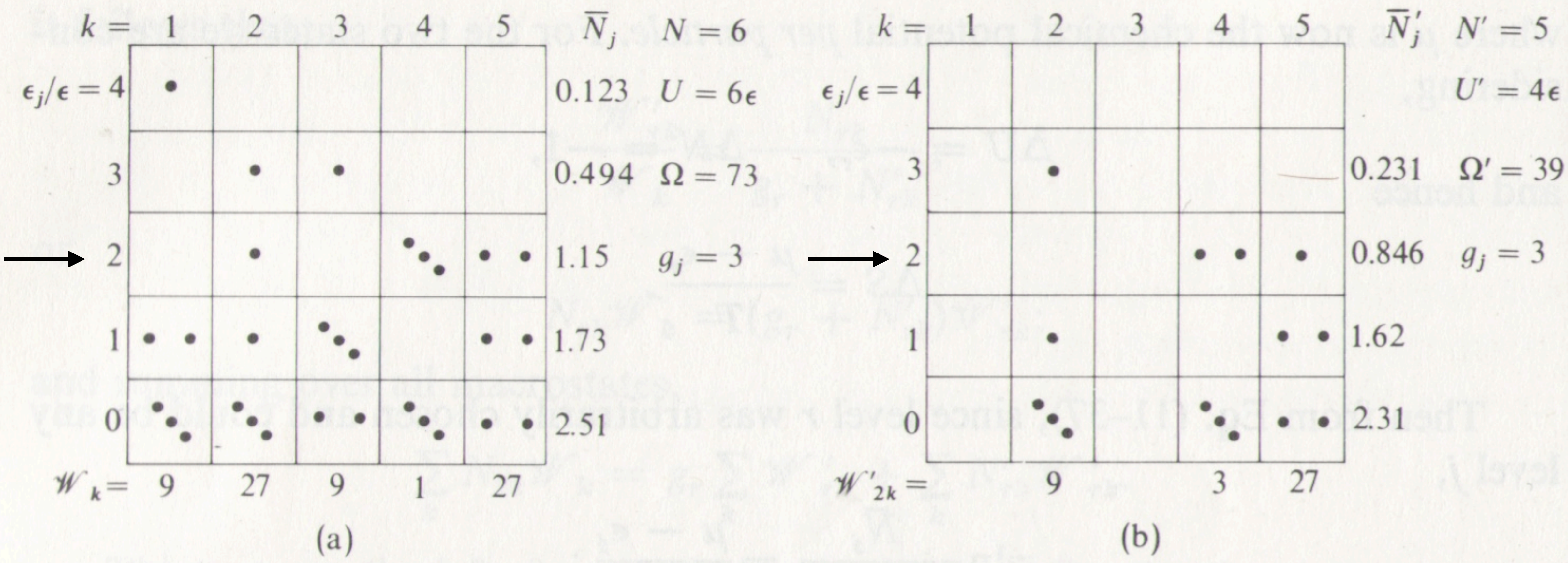


Fig. 11–10 (a) The possible macrostates of an assembly of 6 particles obeying F-D statistics when $U = 6\epsilon$. (b) The possible macrostates when one particle is removed from level 2 of the assembly of part (a). The thermodynamic probability of each macrostate is given at the bottom and the average occupation number of each level is printed on the right of the diagram.

Same setup: system "2" is system "1" with one particle removed from level $r = 2$ with energy $\epsilon_r = 2\epsilon$ (and all other levels kept intact):

$$N'_j \overset{j\neq r}{=} N_j, \qquad N'_r = N_r - 1, \quad U' = U - 2\epsilon = 4\epsilon$$

The probability $\mathcal{W}_k$ of a macrostate k

$$\left.\begin{array}{l} \text{in system "1"} \\ \mathcal{W}_k \;=\; \prod_j \frac{g_j!}{(g_j - N_{jk})!N_{jk}!}, \\ \text{in system "2"} \\ \mathcal{W}'_{rk} \;=\; \prod_j \frac{g_j!}{(g_j - N'_{jk})!N'_{jk}!} \end{array}\right\} \Rightarrow \left\{\begin{array}{l} \frac{\mathcal{W}'_{rk}}{\mathcal{W}_{rk} \;=} \;=\; \frac{(g_j - N_{jk})!N_{jk}!}{(g_j - N'_{jk})!N'_{jk}!} \;=\; \frac{N_{rk}}{g_r - N'_{rk}} \\ \Rightarrow \;\; N_{rk}\mathcal{W}_{rk} \;=\; (g_r - N'_{rk})\mathcal{W}'_{rk} \end{array}\right.$$

Sum over all macrostates :

$$\sum_k N_{rk}\mathcal{W}_k \;=\; g_r \sum_k \mathcal{W}'_{rk} - \sum_k N'_{rk}\mathcal{W}'_{rk} \quad\Rightarrow\quad \Omega \bar{N}_r \;=\; \Omega'(g_r - \bar{N}'_r)$$

$$\Rightarrow \;\; \frac{\bar{N}_r}{g_r - \bar{N}'_r} \;=\; \frac{\Omega'}{\Omega}$$

In macroscopic systems $N_j \gg 1$ so the removal of one particle will make a small change in $\bar{N}_r$

$$\Rightarrow \;\; \frac{\bar{N}_r}{g_r - \bar{N}_r} \;=\; \frac{\Omega'}{\Omega} \;\Leftrightarrow\; \ln \frac{\bar{N}_r}{g_r - \bar{N}_r} \;=\; \ln \Omega' - \ln \Omega \;=\; \frac{\Delta S}{k_B}$$

Since level "r" was arbitrary, for any level j

$$\ln \frac{\bar{N}_j}{g_j - \bar{N}_j} \;=\; \frac{\mu - \epsilon_j}{k_B T} \;\Rightarrow\; \frac{g_j - \bar{N}_j}{\bar{N}_j} \;=\; \frac{g_j}{\bar{N}_j} - 1 \;=\; \exp \frac{\epsilon_j - \mu}{k_B T}$$

$$\Rightarrow \;\; \bar{N}_j \;=\; \frac{g_j}{\exp\left(\frac{\epsilon_j - \mu}{k_B T}\right) + 1}$$ Fermi – Dirac distribution function

Classical distribution function

In many systems $\bar{N}_j \ll g_j \quad \Rightarrow \quad \frac{\bar{N}_j}{g_j \pm \bar{N}_j} \simeq \frac{g_j}{\bar{N}_j} = \exp \frac{\epsilon_j - \mu}{k_B T}$

$\Rightarrow \quad \bar{N}_j = g_j \exp\left(\frac{\mu - \epsilon_j}{k_B T}\right)$ – Classical distribution function.

Maxwell-Boltzmann distribution function

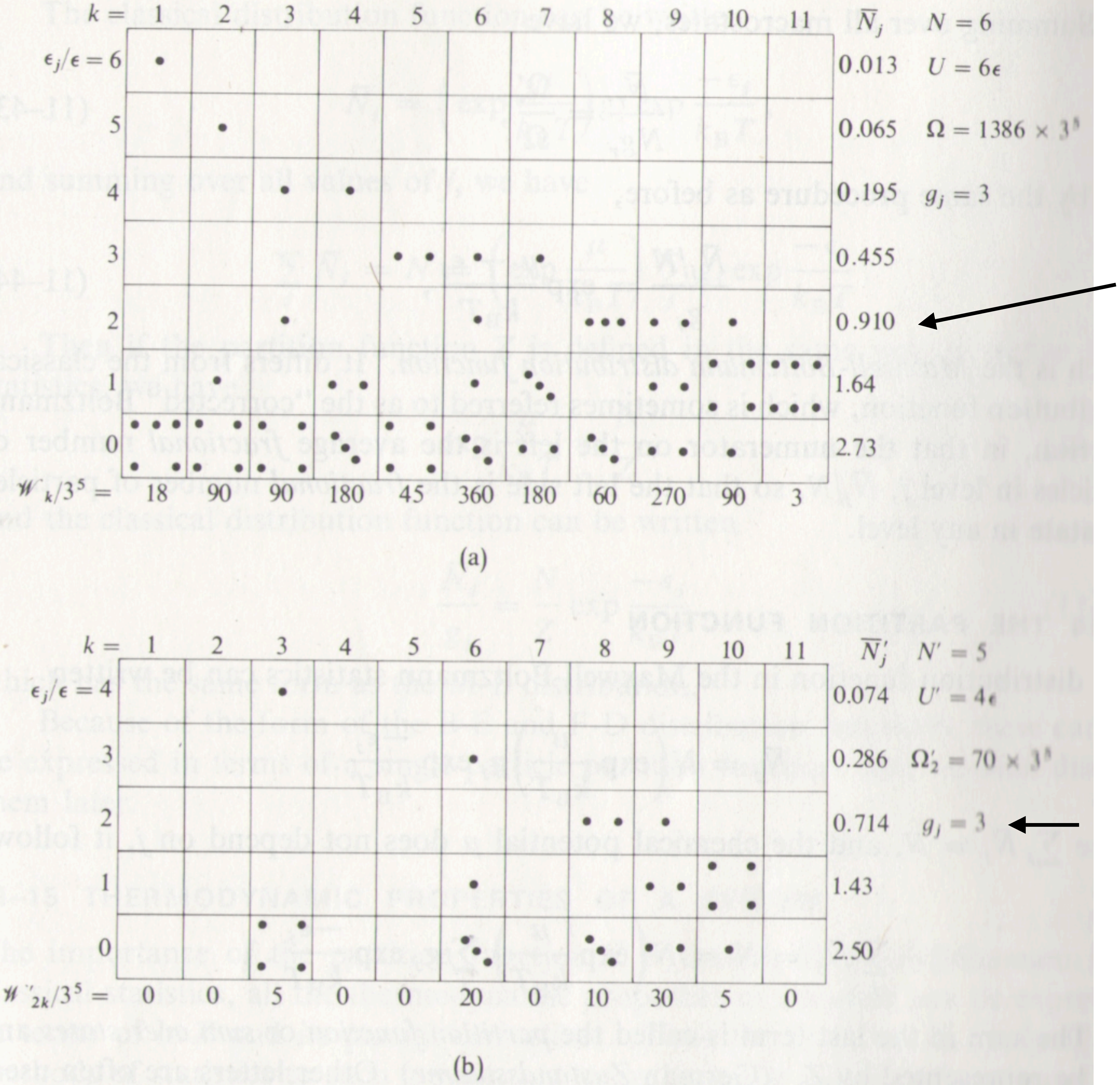


Fig. 11–12 (a) The possible macrostates of an assembly of 6 particles obeying M-B statistics when $U = 6\epsilon$. (b) The possible macrostates when one particle is removed from level 2 of the assembly of part (a). The thermodynamic probability of each macrostate is given at the bottom and the average occupation number of each level is printed on the right of the diagram.

Same setup :
system “2” is system “1”
with one particle
removed from level $r = 2$
with energy $\epsilon_r = 2\epsilon$:

$$N'_j \overset{j\neq r}{=} N_j,$$
$$N'_{rk} = N_{rk} - 1,$$
$$U' = U - 2\epsilon = 4\epsilon$$

The probability $\mathcal{W}_k$
of a macrostate k
in system “1” is

$$\mathcal{W}_k = N! \prod_j \frac{g_j^{N_j}}{N_j!},$$

and in system “2”

$$\mathcal{W}'_k = N'! \prod_j \frac{g_j^{N'_j}}{N'_j!}$$

$$\frac{\mathcal{W}'_{rk}}{\mathcal{W}_k} = \frac{N'!}{N!}\prod_j \frac{g_j^{N'_j}\, N_j!}{g_j^{N_j}\, N'_j!} = \frac{N_{rk}}{N g_r} \quad\Leftrightarrow\quad N_{rk}\mathcal{W}_k = N g_r \mathcal{W}'_{rk}$$

For any level j the sum over all macrostates gives

$$\sum_k N_{jk}\mathcal{W}_k = N g_j \sum_k \mathcal{W}'_{jk}$$

$$\Rightarrow \quad \Omega \bar{N}_j = N g_j \Omega'_j \quad\Leftrightarrow\quad \frac{\bar{N}_j}{N g_j} = \frac{\Omega'_j}{\Omega}$$

$$\Rightarrow \quad \ln\frac{\bar{N}_j}{N g_j} = \ln\Omega'_j - \ln\Omega = \frac{\Delta S}{k_B} = \frac{\epsilon-\mu}{k_B T}$$

$$\Rightarrow \quad \frac{\bar{N}_j}{N} = g_j \exp\frac{\mu-\epsilon_j}{k_B T}$$

Maxwell – Boltzmann distribution

Comparison of distribution functions

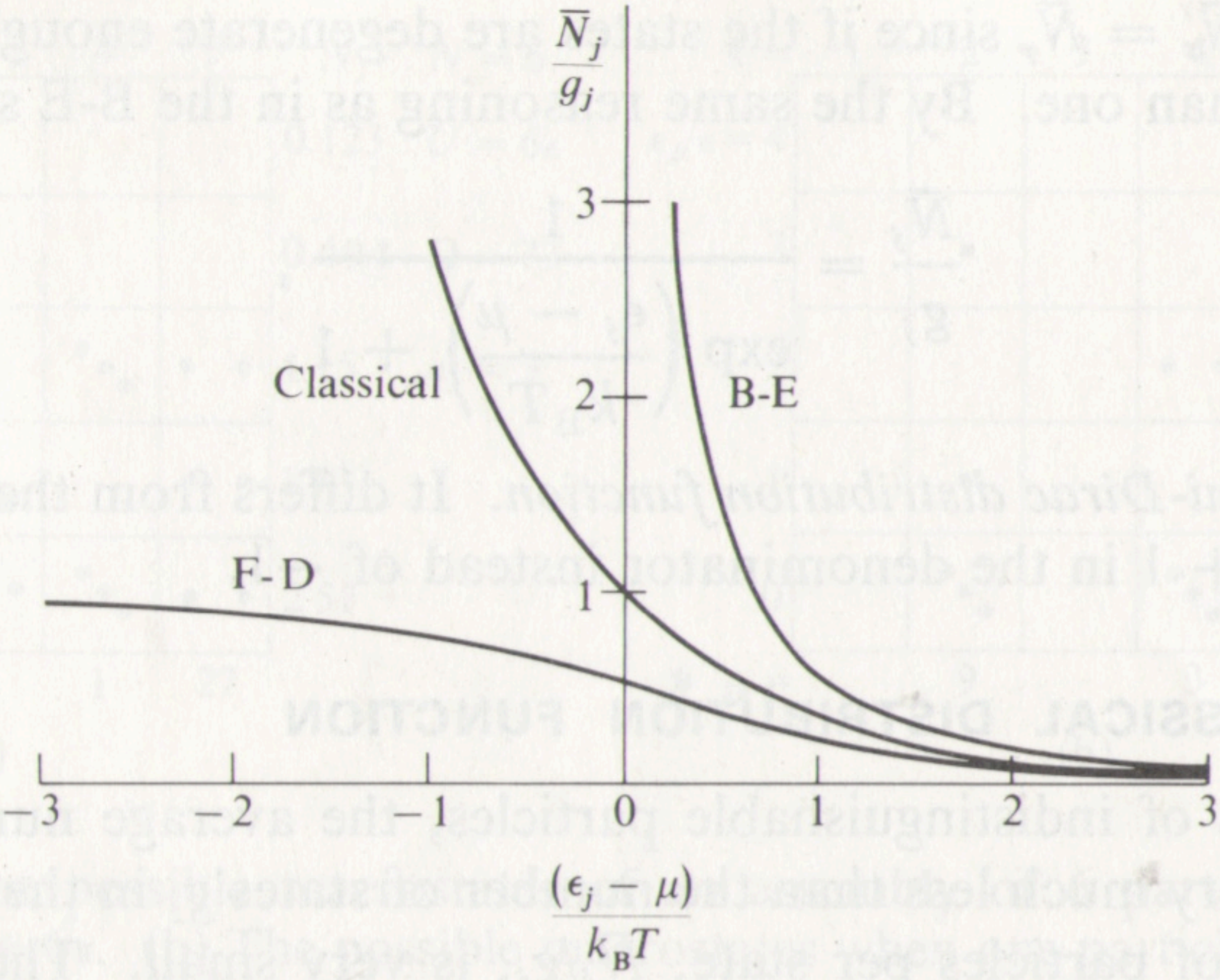


Fig. 11–11 Graphs of the Bose-Einstein, Fermi-Dirac, and classical distribution functions.

$$\bar{N}_j = \frac{g_j}{\exp\left(\frac{\epsilon_j - \mu}{k_B T}\right) + a}$$

$$a = 1 : \ \mathrm{F-D},$$
$$a = -1 : \ \mathrm{B-E},$$
$$a = 0 : \ \mathrm{classical}$$

Temperature is fixed

Partition function

Maxwell-Boltzmann distribution function is $\bar{N}_j = N e^{\frac{\mu}{k_B T}} g_j e^{-\frac{\epsilon_j}{k_B T}}$

Sum over all levels gives

$$\sum_j \bar{N}_j = N = N e^{\frac{\mu}{k_B T}} \sum_j g_j e^{-\frac{\epsilon_j}{k_B T}}$$

$$\text{Partition function :} \quad Z \equiv \sum_j g_j e^{-\frac{\epsilon_j}{k_B T}}$$

In terms of partition function MB distribution looks like

$$\bar{N}_j = g_j \frac{N}{Z} e^{-\frac{\epsilon_j}{k_B T}}, \qquad Z = e^{-\frac{\mu}{k_B T}}$$

Compare to classical distribution

$$\bar{N}_j = e^{\frac{\mu}{k_B T}} g_j e^{-\frac{\epsilon_j}{k_B T}} \Rightarrow \sum_j \bar{N}_j = N = e^{\frac{\mu}{k_B T}} \sum_j g_j e^{-\frac{\epsilon_j}{k_B T}}$$

If we define Z by $Z = N e^{-\frac{\mu}{k_B T}}$

$$\bar{N}_j = g_j \frac{N}{Z} e^{-\frac{\epsilon_j}{k_B T}} \quad - \quad \text{same formula as for MB distribution}$$

Consider system of indistinguishable particles obeying the classical statistics and suppose that energy levels ϵ_j depend on one extensive variable X and do not depend on the corresponding intensive variable Y

$$\left.\begin{array}{ll}\text{Partition function :} & Z(X,T,N) \;=\; \sum_j g_j e^{-\frac{\epsilon_j(X)}{kT}} \\ \text{Chemical potential (per particle) :} & \mu \;=\; kT(\ln Z - lnN) \;=\; \left(\frac{\partial F}{\partial N}\right)_{T,X}\end{array}\right\}$$

$$\left.\begin{array}{l}\Rightarrow \;\; \left(\frac{\partial F}{\partial N}\right)_{T,X} \;=\; -\,kT(\ln Z - \ln N) \\ F \;=\; 0 \;\; \text{at} \;\; N = 0\end{array}\right\} \;\Rightarrow\;\; F \;=\; -\,NkT(\ln Z - \ln N + 1)$$

$$\left.\begin{array}{ll}\text{The entropy} & S \;=\; -\left(\frac{\partial F}{\partial T}\right)_{N,X} \;=\; NkT\left(\frac{\partial \ln Z}{\partial T}\right)_X + Nk(\ln Z - \ln N + 1) \\ \text{The internal energy} & U = F + TS \;=\; NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_X\end{array}\right\} \Rightarrow$$

$$\Rightarrow \;\; S \;=\; \frac{U}{T} + Nk(\ln Z - \ln N + 1)$$

$$Y \;=\; -\left(\frac{\partial F}{\partial X}\right)_{N,T} \;=\; NkT\frac{\partial \ln Z(X,T,N)}{\partial X} \;=\; \Phi(X,T,N) \quad \leftarrow \;\text{equation of state}$$

$\Rightarrow$ Thermodynamical properties are completely defined by $Z(X,T,N)$

Gibbs function $G = \mu N = -NkT(\ln Z - \ln N)$

Recall $G = U - TS + YX = F + YX \Rightarrow YX = G - F$

$$\left.\begin{aligned} G &= \mu N = -NkT(\ln Z - \ln N) \\ F &= -NkT(\ln Z - \ln N + 1) \end{aligned}\right\} \Rightarrow YX = G - F = NkT$$

For the P − V system $YX = NkT$ means $PV = NkT$

$\Rightarrow$ The constant k in the equation $S = k \ln \Omega$ is $k = k_B = \frac{R}{N_A}$

Monoatomic ideal gas

System: *N* identical indistinguishable molecules each of mass *m.*
Except for very low temperatures, such system can be described by *classical statistics*

$$\text{Partition function :} \quad Z(X,T,N) \;=\; \sum_j g_j e^{-\frac{\epsilon_j(X)}{kT}}$$

$$\epsilon_j \;=\; \frac{\pi^2\hbar^2 n_j^2}{2mV^{\frac{2}{3}}} \qquad \text{for particles in the box of volume } V$$

$$\Rightarrow\; Z(V,T,N) \;=\; \sum_j \sum_{n_j} g_j e^{-\frac{\pi^2\hbar^2}{2mkT} n_j^2 V^{-\frac{2}{3}}}\,, \qquad \vec{n}_j \equiv (n_x, n_y, n_z)$$

For large volume and large number of particles we can replace the sum by the integral

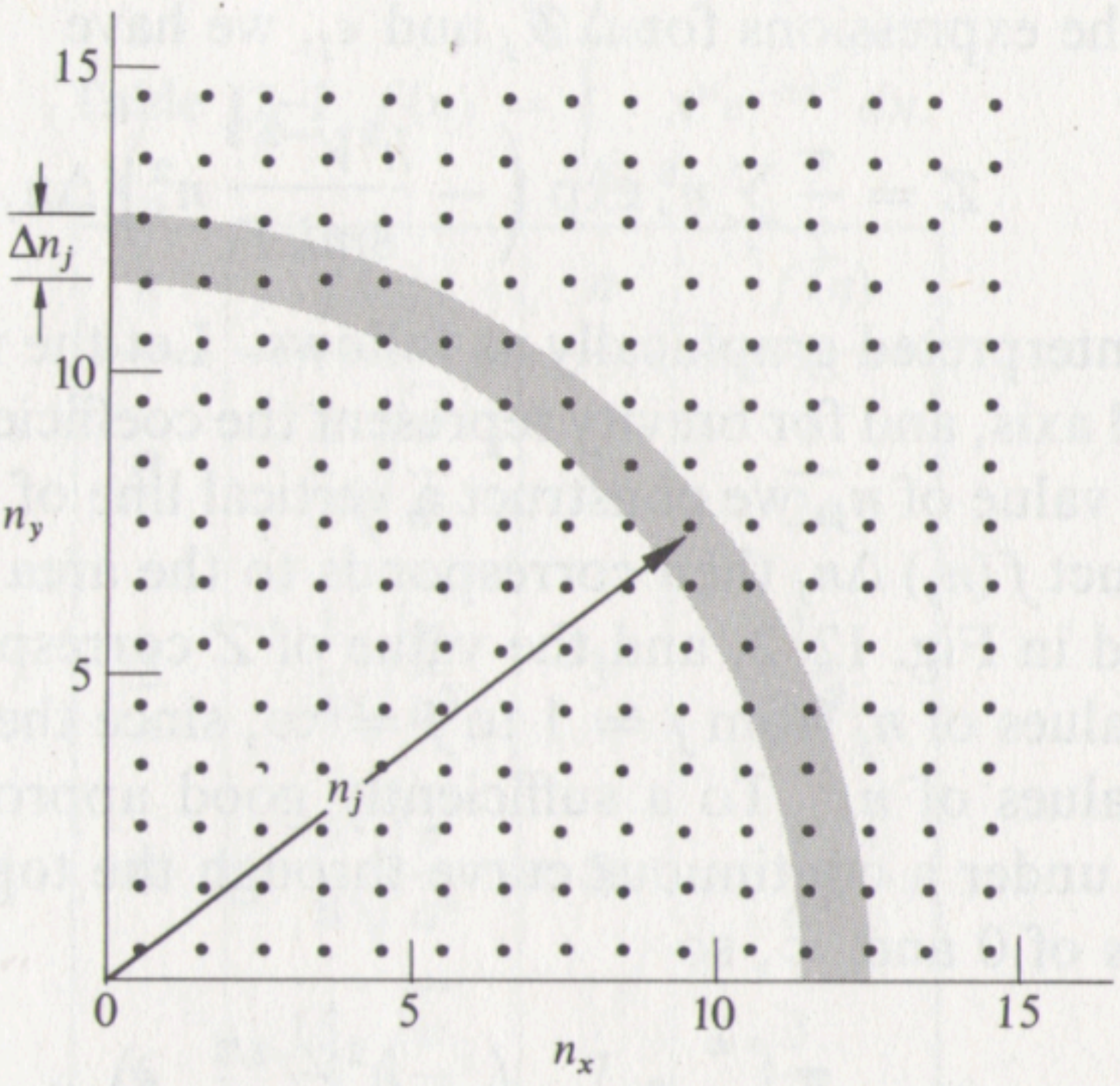


Fig. 12–1 Quantum states in *n*-space.

Number of states in the shaded area between n_j and $n_j + \Delta n_j$:

$\frac{\pi}{2} n_j^2 \Delta n_j$

$$\Rightarrow \sum_j \sum_{n_j} g_j \rightarrow$$

$$\rightarrow \sum_j \frac{\pi}{2} n_j^2 \Delta n_j$$

$$Z = \frac{\pi}{2} \sum_j n_j^2 \Delta n_j \times e^{-\frac{\pi^2 \hbar^2}{2mkT} n_j^2 V^{-2/3}}$$

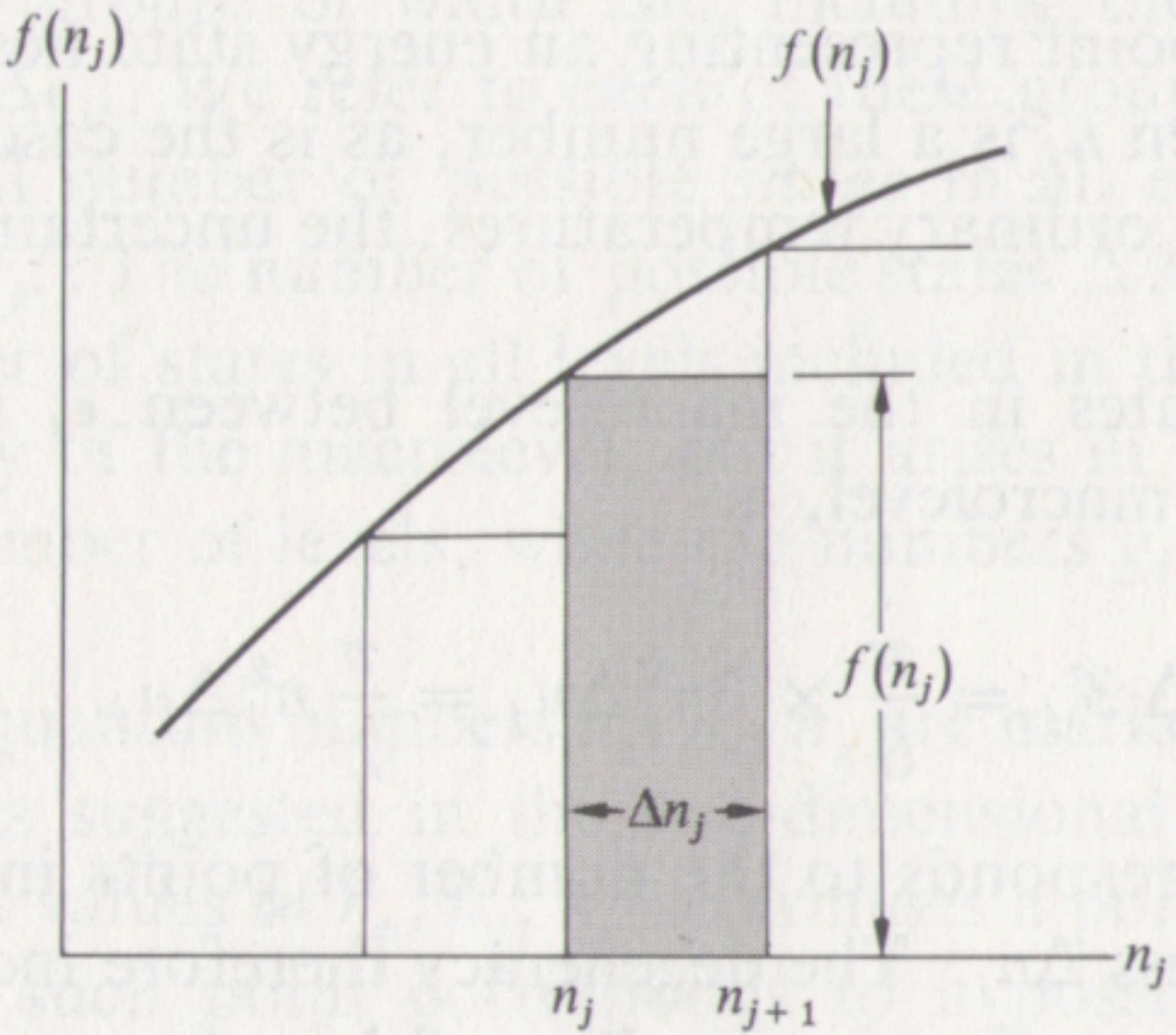


Fig. 12–2 The partition function Z is equal to the total area under the step function, and is very nearly equal to the area under the continuous curve.

$$\sum_j \Delta n_j f(n_j) \rightarrow$$

$$\rightarrow \int_0^\infty f(n_j) dn_j$$

$$Z = \frac{\pi}{2}\int_0^\infty dn_j \; n_j^2$$

$$\times \; e^{-\frac{\pi^2\hbar^2}{2mkT} n_j^2 V^{-2/3}}$$

$$= V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$$

$$Z = V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$$

$$Y = NkT\frac{\partial \ln Z(X,T,N)}{\partial X} \Leftrightarrow P = NkT\frac{\partial \ln Z(V,T,N)}{\partial V}$$

$$\frac{\partial \ln Z(V,T,N)}{\partial V} = \frac{1}{V} \Rightarrow P = \frac{NkT}{V} = \frac{nRT}{V} \Rightarrow PV = nRT$$

The internal energy $U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{3}{2}NkT$

$$\Rightarrow U = \frac{3}{2}nRT \Rightarrow C_V = \frac{3}{2}nR \Leftrightarrow c_v = \frac{3}{2}R$$

The entropy

$$S = \frac{U}{T} + Nk(\ln Z - \ln N + 1) = Nk\left[\frac{5}{2} + \ln\frac{V}{N} + \frac{3}{2}\ln\frac{mkT}{2\pi\hbar^2}\right]$$

$$\Rightarrow$$

$$s = c_v \ln T + R\ln V + R\left[\frac{3}{2}\ln\frac{mk}{2\pi\hbar^2} - \ln N + \frac{5}{2}\right]$$

Sacker – Tetrode equation for the absolute entropy of monoatomic gas