BEYOND THIS POINT BE DRAGONS

BEYOND THIS POINT BE EQUATIONS!

Some things to know from the prerequisites:

- **First Year Chemistry**
  - Significant figures
  - Manipulation of units
  - Fundamental units and derived units
  - The Ideal Gas Law
  - Van der Waals Gas Law
  - Enthalpy
  - Entropy
  - Free Energy
  - Hess's Law
  - Equilibrium Coefficients
  - Activity

Some things to know from the prerequisites (continued):

- **First Year Calculus (and High School Math)**
  - How to manipulate an equation algebraically
  - Derivatives of one variable
  - Integrals of one variable
  - Power series
  - Properties of logarithms and exponentials

What is Physical Chemistry?

- Physics of Chemistry

What is Thermodynamics?

- **THERMO** - heat, energy
- **DYNAMICS** - changes
- Consider

$$pV = nRT$$

  - Rewrite as:

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

- What can cause p to change?
  - V - volume

$$\left(\frac{\partial p}{\partial V}\right)_{n,T} = -\frac{nRT}{V^2}$$

  - n - number of moles of gas

$$\left(\frac{\partial p}{\partial n}\right)_{V,T} = \frac{RT}{V}$$

  - T - temperature

$$\left(\frac{\partial p}{\partial T}\right)_{n,V} = \frac{nR}{V}$$

How do we describe the change if all three are changing at once?

$$dp = \left(\frac{\partial p}{\partial V}\right)_{n,T} dV + \left(\frac{\partial p}{\partial n}\right)_{V,T} dn + \left(\frac{\partial p}{\partial T}\right)_{n,V} dT$$

- Note carefully the difference between ∂ and d:
    - ∂ describes the partial change due to the change in a particular variable.
    - d describes the total change.
- Some other ways of describing changes (useful for numerical applications):
    - Δ - a finite change.
    - δ - an infinitesimal change.

UNITS

- Even when represented by a symbol, physical quantities have units.
  - Verification of units can help detect mistakes in a derivation.
- p - force per unit area. The SI unit is the Pascal (Pa).
  - 1 Pa $=$ 1 N m^{-2} $=$ 1 kg m s^{-2} m^{-2}
  - 1 Pa $=$ 1 kg m^{-1} s^{-2} (fundamental units)
- V - volume
  - m^3 (fundamental units)
- n -number of moles
  - mol (fundamental units)

- R - Gas Constant
  - 8.314 J K^{-1} mol^{-1} $=$ 8.314 kg m^2 s^{-2} K^{-1} mol^{-1}
  - (1 J $=$ 1 kg m^2 s^{-2} (fundamental units))
  - (1 J $=$ 1 Pa m^3 or 1 Pa $=$ 1 J m^{-3})
- T K (fundamental units)
  - temperature is on absolute Kelvin scale.

UNITS ARE YOUR FRIENDS!!

EQUATIONS OF STATE

- “An equation of state is the mathematical relationship among the relevant thermodynamic variables of an equilibrium system.”
- Examples (from gas behaviour):
    - Ideal Gas Equation of State

$$pV = nRT$$

    - van der Waals Equation of State

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

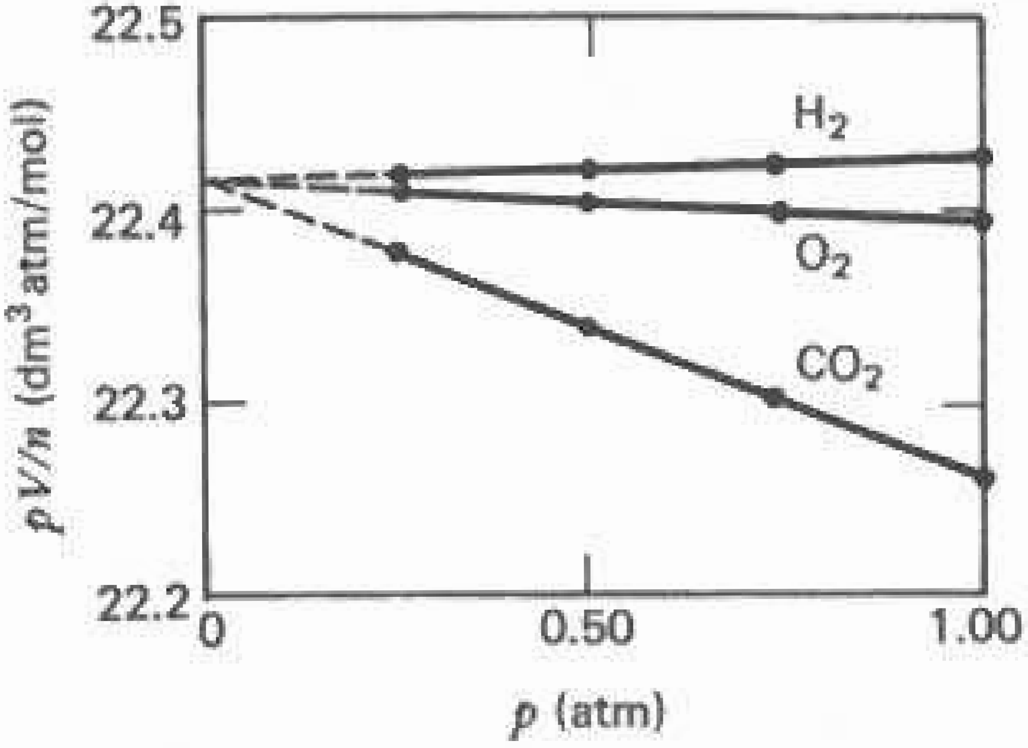


Figure 21.1 The *pV* product for three gases, showing the universal approach to the ideal gas value as the pressure tends to zero. From R. H. Cole and J. S. Coles, *Physical Principles of Chemistry* (Freeman, San Francisco, 1964).

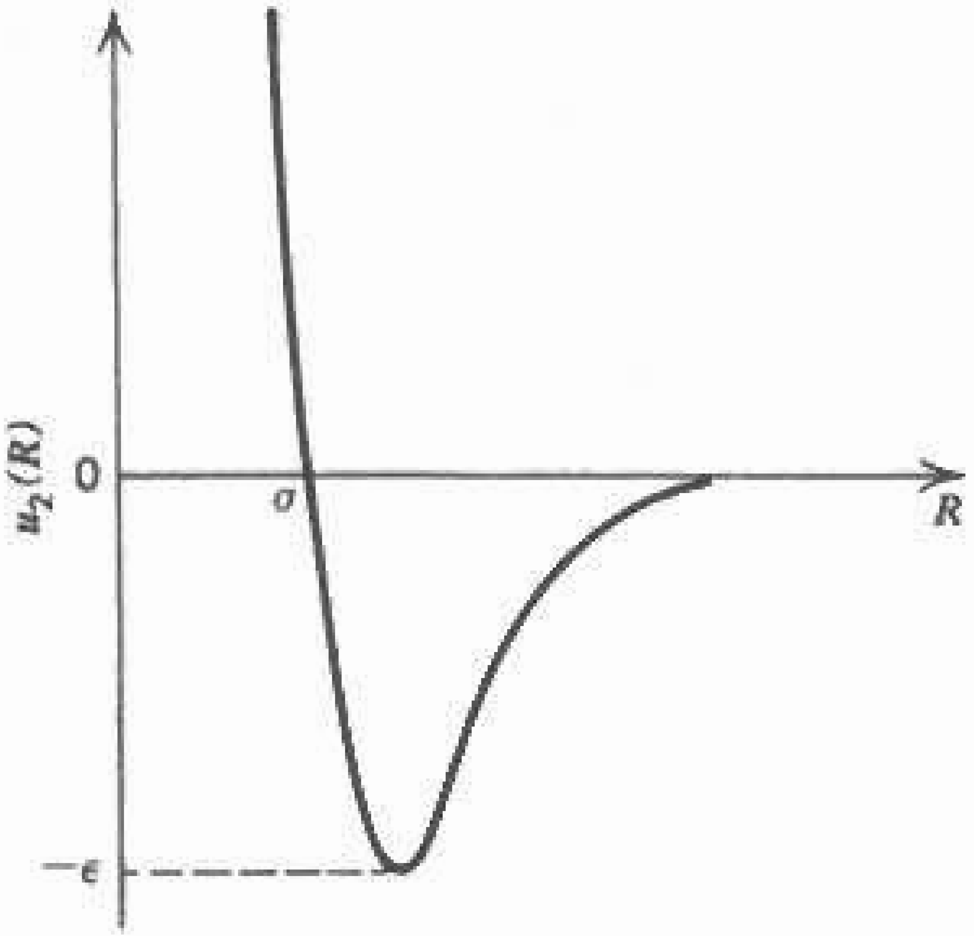


Figure 21.6 A representation of the intermolecular potential between a pair of molecules as a function of the distance between them.

- Berthelot Equation of State

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{T\overline{V}^2}$$

- Virial Equation of State

$$\frac{p\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^2} + \ldots$$

THERMODYNAMIC VARIABLES

- Intensive
- Extensive
- Relation to Equation of State
- Description of Equilibrium

COMPRESSIBILITY

- Recommended Reading: Chapter 21 of Berry *et al.*
- The compressibility factor, Z, may be defined:

$$Z \equiv \frac{\overline{V}(\text{real})}{\overline{V}(\text{ideal})} = \frac{p\overline{V}}{RT}$$

- Ideal gas

$$Z \equiv \frac{p\overline{V}}{RT} = 1$$

- van der Waals

$$Z \equiv \frac{p\overline{V}}{RT} = \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}}$$

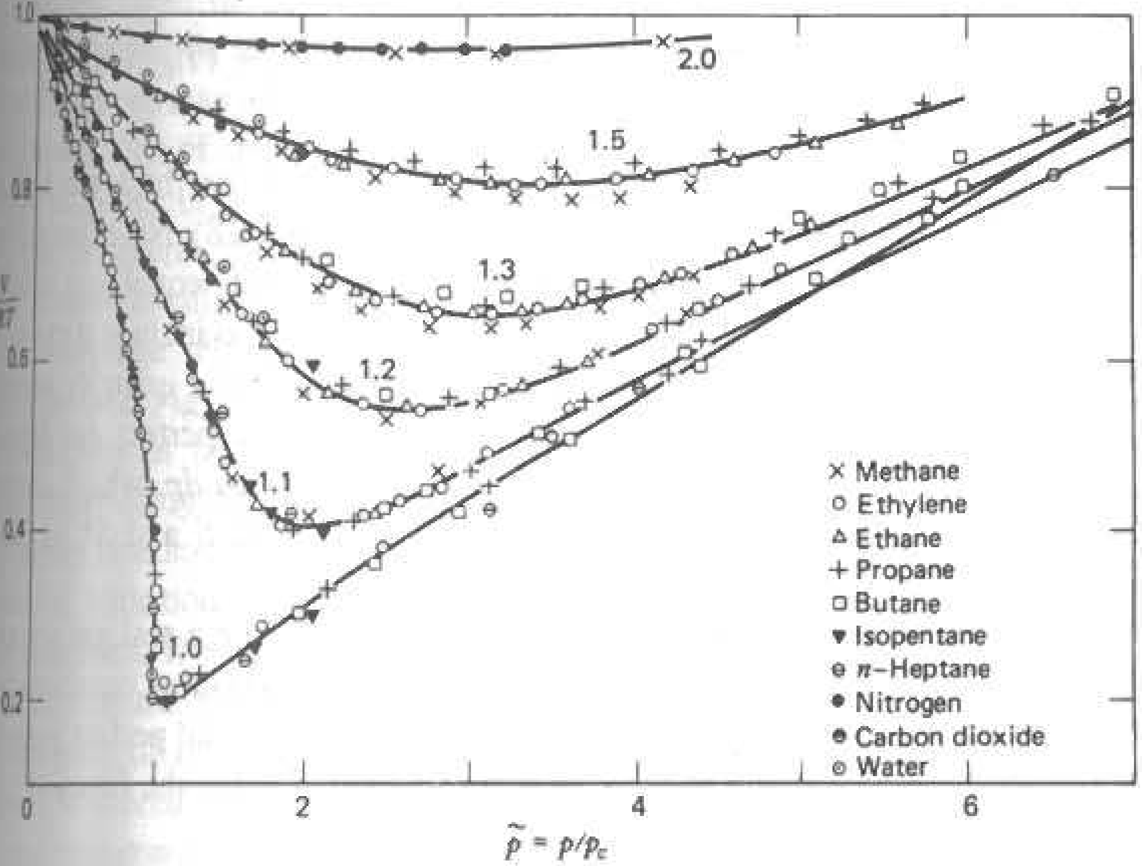


Figure 21.5 The compressibility factor pV/nRT for several gases plotted as a function of the reduced pressure p/p_c. The curves are for different values of T/T_c. From G. J. Su, *Ind. Eng. Chem.* **38,** 803 (1946).

- Virial equation

$$Z \equiv \frac{p\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^2} + \ldots$$

- For more equations of state, see Table 21.2 on page 553 of Berry *et al.*
- Deviation from 1 of the value of Z, the compressibility factor, is a measure of the nonideal behaviour of a gas.
- $B(T)$, the second virial coefficient, has units of molar volume (m^3 mol^{-1}) and is the first term in the description of deviation from ideal behaviour.
- $C(T)$, the third virial coefficient, has units of the square of molar volume (m^6 mol^{-2}) and is the second term in the description of deviation from ideal behaviour.

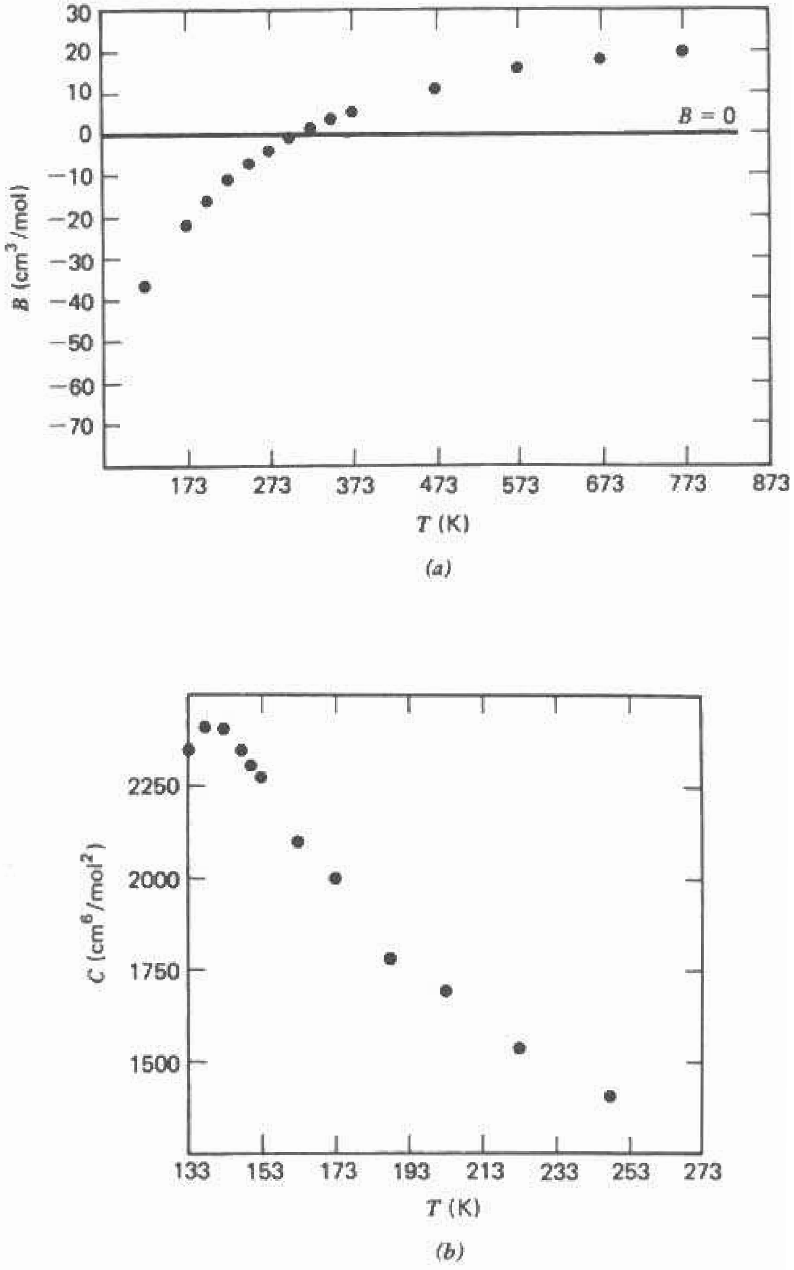


Figure 21.7 The second and third virial coefficients of Ar.

Significance of the second virial coefficient, $B(T)$

- $B(T)$ is temperature dependent
  - At high T repulsions are expected to be important.
  - At low T attractions are expected to be important.
- Consider the van der Waals equation of state written in virial form:

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \frac{b^2}{\overline{V}^{\,2}} + \ldots$$

or:

$$Z \equiv \frac{p\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^{\,2}} + \ldots$$

where:

$$B(T) = b - \frac{a}{RT} \;;\quad C(T) = b^2$$

- If T is large, $B(T) \rightarrow b$, which is positive.
    - Repulsion accounts for most of the deviation from ideal behaviour.
- If T is small, $B(T)$ becomes negative.

$$B(T) \rightarrow -\frac{a}{RT}$$

-
    - Attraction accounts for most of the deviation from ideal behaviour.
- When $B(T) = 0$, the corresponding temperature is the Boyle temperature, T_B.

$$B(T) = 0 = b - \frac{a}{RT_B}; T_B = \frac{a}{Rb}$$

- A physical interpretation of the Boyle temperature, T_B, is that temperature at which the average attractive and repulsive forces are balanced.
- The second virial coefficient depends on the interaction potential between molecules of the gas of interest.
  - See section 21.7 of Berry *et al.*
- For a van der Waals gas, the Boyle temperature, T_B, allows us to define a dimensionless temperature scale in terms of multiples of the Boyle temperature.

$$B(T) = 0 = b - \frac{a}{RT_B}$$

- Dividing both sides of the equation by b gives:

$$\frac{B(T)}{b} = 1 - \frac{a}{RbT} = 1 - \frac{T_B}{T}$$

- This means:
  - that any temperature can be expressed as a multiple of of the Boyle temperature, T_B;
  - and that the second virial coefficient, $B(T)$, can be expressed as a multiple of the second van der Waal's parameter b.
- Dimensionless scales allow the convenient comparison of a number of different gases described by the van der Waals equation.
- To set up scales of $\overline{V}$ and P, combinations of parameters that have the "right" dimensions are need.
  - The van der Waals parameter b have units of molar volume, which are the same units as $\overline{V}$.
  - The term $a/\overline{V}^2$ has the same units are pressure.

- Thus, one system of scaled variables is:
    - $\mathcal{T} = \frac{T}{T_B} = \frac{RbT}{a}$
    - $\mathcal{V} = \frac{\overline{V}}{b}$
    - $\mathcal{P} = \frac{pb^2}{a}$
- The van der Waals equation may be rewritten as:

$$\mathcal{P} = \frac{\mathcal{T}}{\mathcal{V} - 1} - \frac{1}{\mathcal{V}^2}$$

- This contains the same information as the original form of the van der Waals equation:

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

- Consider $p\overline{V}$ isotherms of the van der Waals equation.
    - At high temperature, the curve has neither a maximum nor a minimum.
    - At lower temperature, the curve has both a maximum and a minimum.
    - As temperature is increased from this lower temperature, the maximum and minimum move closer together.
    - There exists a temperature such that the minimum and maximum meet in an inflection point.
        - This temperature is the critical temperature.
    - An inflection point has the properties that the first and second derivatives of the curve are 0.

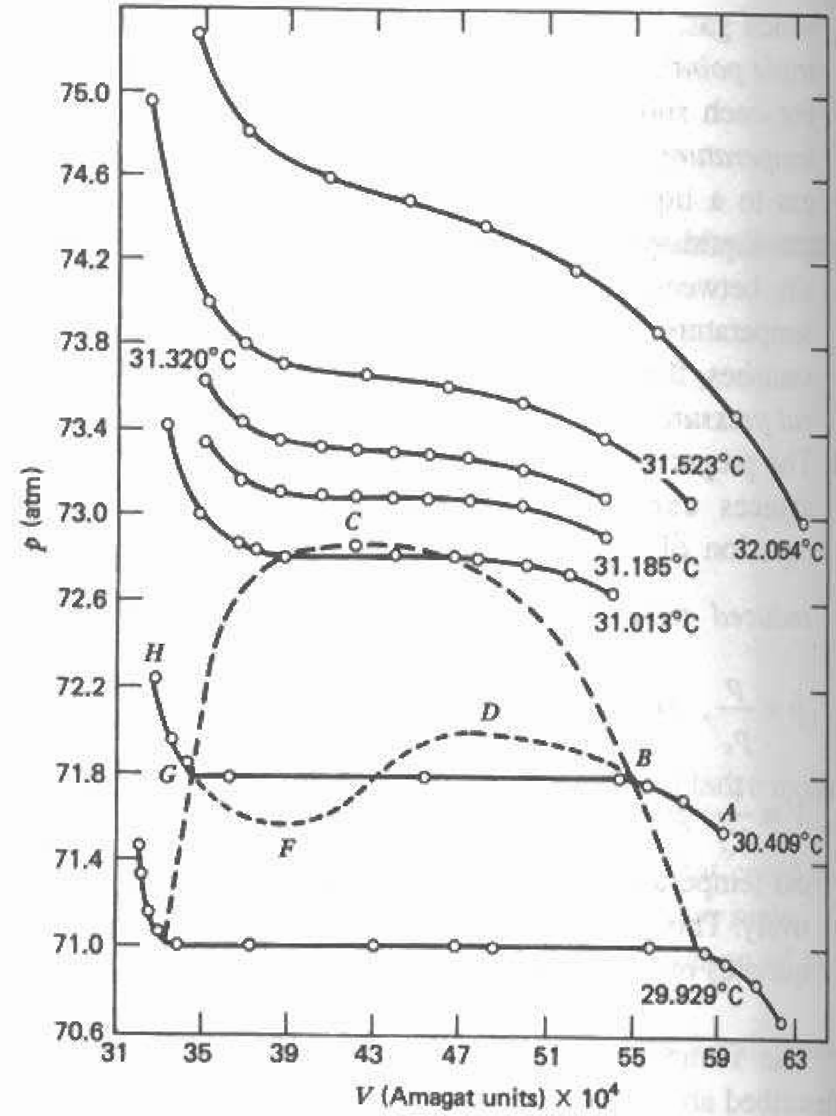


Figure 21.3 Some isotherms of CO_2 in the immediate vicinity of the critical temperature. From E. A. Moelwyn-Hughes, *Physical Chemistry* (Cambridge University Press, Cambridge, 1940); data from A. Michels, B. Blaisse, and C. Michels, *Proc. Roy. Soc.* **A160,** 367 (1937). One Amagat unit of volume for CO_2 is 2.2398×10^4 cm³/mol.

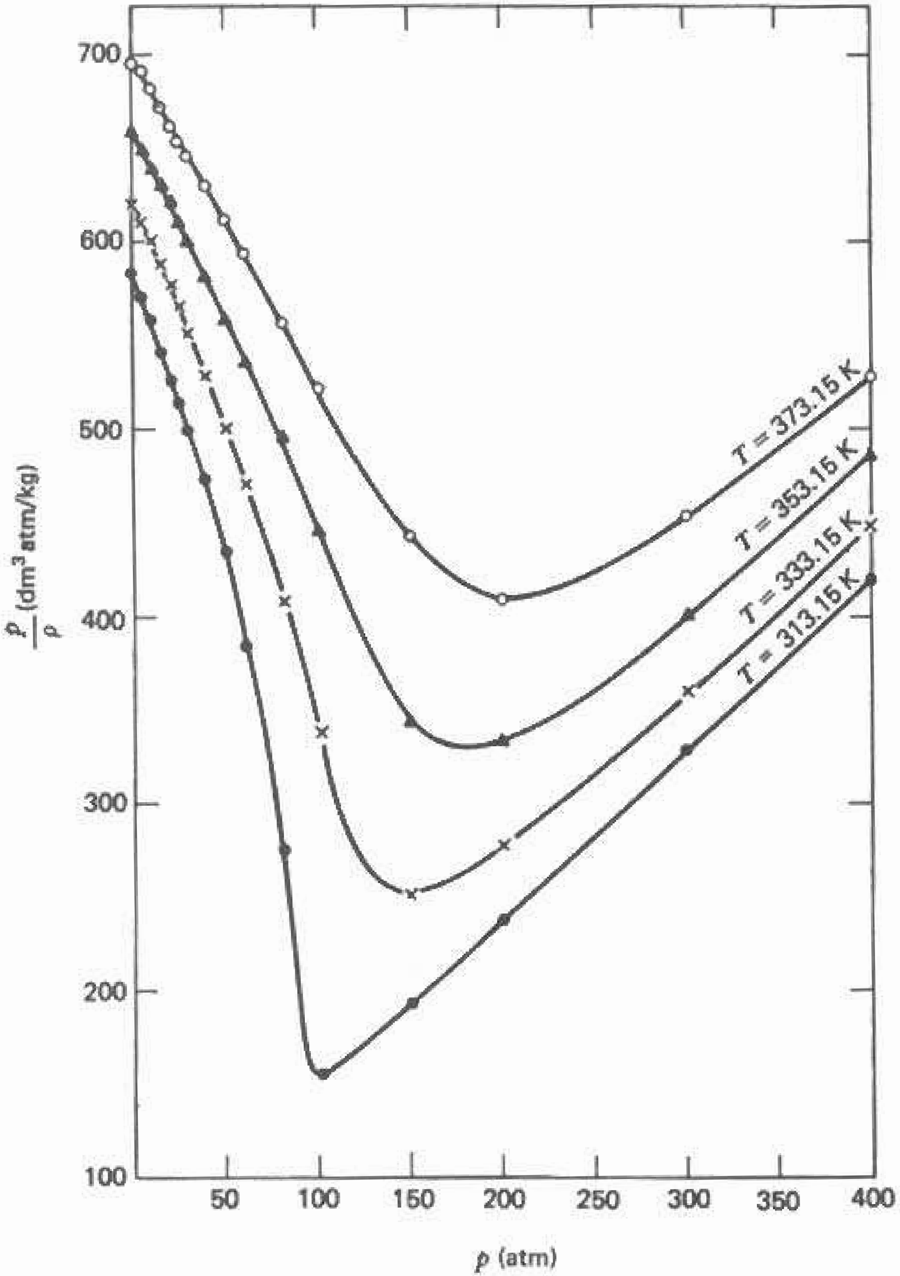


Figure 21.2 Some isotherms of CO_2 for temperatures above the critical temperature.

- Thus there are three simultaneous equations that can be solved for p_c, T_c, and $\overline{V}_c$.

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

$$\left(\frac{\partial p}{\partial \overline{V}}\right)_{T=T_c} = 0 = \frac{-RT}{(\overline{V} - b)^2} + \frac{2a}{\overline{V}^3}$$

$$\left(\frac{\partial^2 p}{\partial \overline{V}^2}\right)_{T=T_c} = 0 = \frac{2RT}{(\overline{V} - b)^3} - \frac{6a}{\overline{V}^4}$$

- To solve for $(p_c, \overline{V}_c, T_c)$:
  - Isolate T_c in the first and second derivatives.
  - Combine the resulting two equations and isolate $\overline{V}_c$

- Continued:
    - Substitute $\overline{V}_c$ into one of the equations and evaluate T_c.
    - Substitute $\overline{V}_c$ and T_c in the van der Waals equation to get p_c.
    - This gives:

$$\overline{V}_c = 3b; \quad T_C = \frac{8a}{27Rb}; \quad p_C = \frac{a}{27b^2}$$

- The critical variables provide another way to scale $(p, \overline{V}, T)$. (See section 21.1 of Berry *et al.*)
- The resulting set of scaled variables are known as *the reduced variables*, $(\tilde{p}, \tilde{V}, \tilde{T})$.
- Different gases described by the same set of reduced variables are in *corresponding states*.

- Something to try on your own (between now and the first term test):
  - Write the van der Waals equation in terms of reduced variables.

Some useful properties of partial derivatives

- Consider some function $z(x, y)$.

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y^{-1}$$

if z is a continuous function of x.

  - Most thermodynamic functions are continuous functions.
- An application of this would be for a van der Waals gas of the evaluation $\left(\partial \overline{V}/\partial p\right)_T$.

The Cyclic Rule

- Another useful property of partial derivatives.
- Again consider the function $z(x, y)$. The cyclic rule is:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

- This in combination with the previous property allows us to find one of the derivatives given the other two.
- An application of this would be the evaluation for a van der Waals gas of

$$\left(\frac{\partial \overline{V}}{\partial T}\right)_p$$

- The cyclic rule is a consequence of the chain rule.

The Chain Rule

- Consider function $f(x_1, x_2)$ such that
    - $x_1 = x_1(y_1, y_2)$
    - $x_2 = x_2(y_1, y_2)$
- Then the chain rule is:

$$\left(\frac{\partial f}{\partial x_1}\right)_{x_2} =$$

$$\left(\frac{\partial f}{\partial y_1}\right)_{y_2}\left(\frac{\partial y_1}{\partial x_1}\right)_{x_2} + \left(\frac{\partial f}{\partial y_2}\right)_{y_1}\left(\frac{\partial y_2}{\partial x_1}\right)_{x_2}$$

- Consider the case where

$$x_1 = T,\ x_2 = p,\ y_1 = T,\ y_2 = V$$

- Then the chain rule becomes:

$$\left(\frac{\partial f}{\partial T}\right)_p = \left(\frac{\partial f}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial f}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

- If $f = p$ then this becomes:

$$0 = \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

- From this the cyclic rule may be derived:

$$-\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

- which can be rearranged as:

$$-1 = \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V$$

State Functions and Path Functions (see Chapter 13 of Berry)

- Consider a system initially at equilibrium in state 1.
- The system undergoes a change and comes to a new equilibrium at state 2.
- The value of a **state function** at state 2 is **independent of the path** taken from state 1 to state 2.
- The value of a **path function** at state 2 is **dependent on the path** taken from state 1 to state 2.

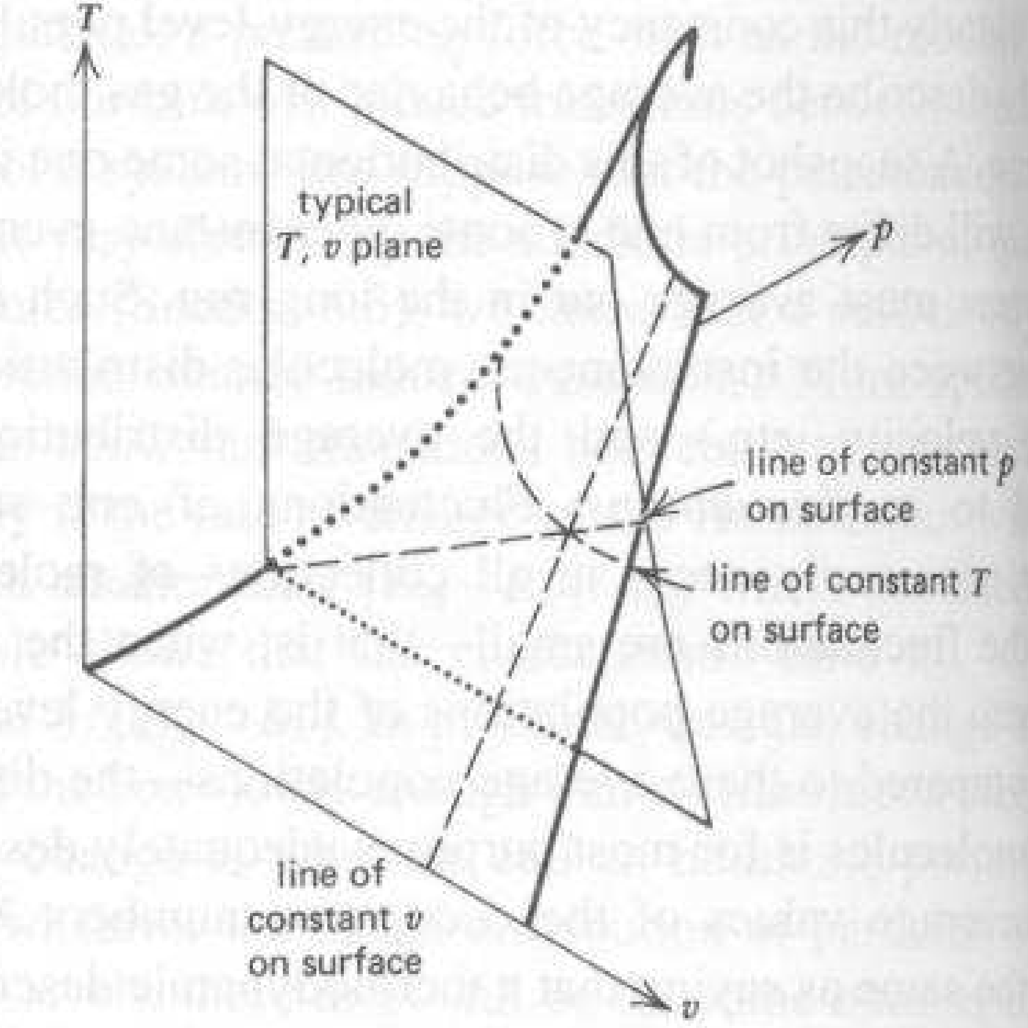


Figure 13.1 Part of a surface representing the equation of state in (p, v, T) space. The particular surface shown is for the perfect gas, with the equation of state $pv = RT$. The lines of constant p, T, and v on the surface are the loci of the intersections of the surface with typical (T, v), (p, v), and (T, p) planes, respectively. A typical (T, v) plane is shown; the others are omitted for clarity.

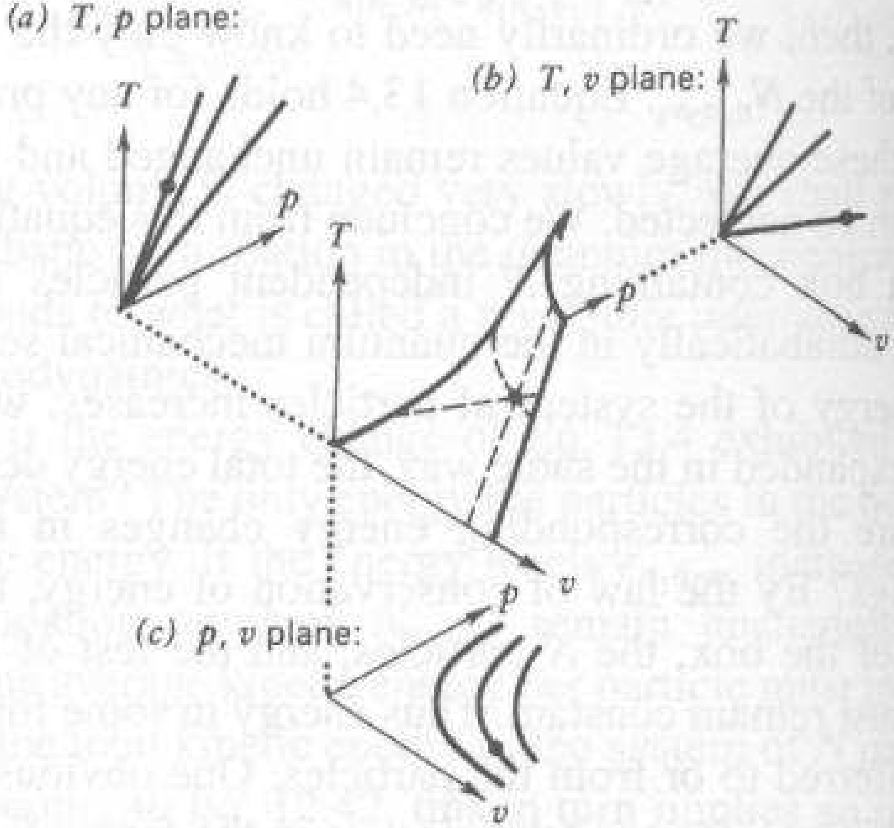


Figure 13.2 Intersections of the perfect gas surface of Fig. 13.1 with planes on which v, p, or T is constant. (a) (T, P) plane—each line in this plane is the locus of the intersection of the p, v, T surface and a plane on which v is constant. (b) (T, v) plane—each line in this plane is the locus of the intersection of the p, v, T surface and a plane on which p is constant. (c) (p, v) plane—each curve (hyperbola) in this plane is the locus of the intersection of the p, v, T surface and a plane on which T is constant.

Exact and Inexact Differentials

- An infinitesimal change on a path for a state function between state 1 and state 2 is described by an exact differential.
- An infinitesimal change on a path for a path function between state 1 and state 2 is described by an inexact differential.
- Consider some function z such that:

$$dz = f_x(x,y)dx + f_y(x,y)dy$$

where functional forms are chosen arbitrarily for f_x and f_y. For example:

$$f_x(x,y) = xy \text{ and } f_y(x,y) = x^2y^2$$

- Does there exist some function $z(x, y)$ such that dz is the total derivative?
  - If there does, then z is a state function.
  - If there does not, then z is a path function.

How to Test for State Functions

- If z is a state function, it must pass the cross derivative equality test.
- If the state function $z(x, y)$ exists then:

$$\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) = \left(\frac{\partial^2 z}{\partial x \partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \left(\frac{\partial^2 z}{\partial y \partial x}\right)$$

- Applied to $dz = f_x(x, y)dx + f_y(x, y)dy$, the test becomes whether:

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

- Applied to $dz = xydx + x^2y^2dy$, we see that the cross derivative equality test is failed because:

$$\frac{\partial xy}{\partial y} = x$$

and

$$\frac{\partial (x^2y^2)}{\partial x} = 2xy^2$$

Therefore in this case z is a path function.

Energy, Work, and Heat

- Consider energy and molecules.
  - Energy affects how molecules react. In particular the distribution of energy within a molecule influences how it behaves both chemically and physically.
- How do molecules have energy?
  - In chemical bonds. The more energy required to break a bond, the stronger the bond is.
  - In internal motions (such as vibration and rotation) and electronic excitations.
  - As kinetic energy of motion. Temperature is a way of measuring the average kinetic energy of a system of molecules at equilibrium.

Energy (from a Thermodynamic Perspective)

- Consider the exothermicity of a chemical reaction.
  - Food Calories
  - Fuel Combustion
  - Corrosion
  - Decomposition
- Energy is considered on a scale related to changes, not an absolute scale.
- In thermodyamics, two particular forms of energy transfer are considered:
  - q heat
  - w work

What is energy?

- What are the properties of energy?
  - Cannot be created or destroyed
  - Can only change form such as be converted to heat, work, or internal energy.
- This will be examined initially from the perspective of the perfect gas.

The Perfect Gas (See Chapter 12 of Barry)

- A dilute gas is the simplest type of matter.
  - Molecules are far apart.
  - Molecules do not interact with one another.
  - Properties observed are related to the properties of the individual gas molecules.
  - An ideal gas is a perfect gas.

- In the limit of low pressure, real gases behave as perfect gases.
- The behaviour of a substance is described the equation of state.
  - The equation of state relates p, $\overline{V}$, and T.
  - Empirically determined for real substances.

The Kinetic Hypothesis

- The kinetic hypothesis assumes:
  - Individual molecules are continually in motion, even if the system as a whole is not in motion.
  - Individual motions are in all directions.
  - Individual motions are at a variety of speeds.
- The net effect is that the contributions of the individual molecules tend to cancel.

- Two consequences of molecular motion:
  - Kinetic energy of individual molecules contributes to the internal energy of the system.
  - The impact of the moving molecules on the wall of the container contributes to the pressure exerted by the system on the surroundings.
- In a dilute gas only the internal energy and pressure need to be considered at present.
- Consider the case of a monatomic gas such as He, Ne, or Ar.
  - No motions of the atoms internal to the molecule need to be considered.
  - Motions of the molecules are independent
  - Molecules exert no forces on each other, except at impact.

- Continued:
  - Collisions are elastic with momentum and kinetic energy being conserved.
  - If the extremely remote possibility of electronic excitation of the atom is ignored, then such a gas may be referred to as perfect.
- Most real gases at moderate pressures (such as atmospheric) are sufficiently dilute to behave as perfect gases.
- A perfect gas is also assumed to be at equilibrium.
  - Macroscopic properties of the system are not observed to change with time.
  - Even though macroscopic properties of the system are stable, the microscopic positions and velocities of the individual molecules are constantly changing.

- Continued:
  - Many different microscopic states (“microstates”) can correspond to one particular macroscopic state (“macrostate”).
  - Macroscopic properties such as p and T are related to averages of microscopic velocities.
  - In a particular macrostate, the values of the microscopic variables fluctuate negligibly about their average values.
  - Thus the equilibrium distribution of microscopic velocities is invariant with time.
- At equilibrium, in the absence of an external field, a gas is uniform throughout its container and the gas is at rest in its container with no flows or currents.

- Continued:
    - Measurements of intensive variables such as pressure and temperature are the same regardless of where in the system they are made.
    - Kinetic energy per unit volume is the same in every volume element (that is sufficiently large to contain very many molecules).
        - Thus the distribution of velocities is the same everywhere.
- If the gas as a whole is at rest then:

$$< \mathbf{v} >= \frac{1}{N}\sum_{i=1}^{N}\mathbf{v}_i = 0 \text{ and thus } \sum_{i=1}^{N}\mathbf{v}_i = 0$$

- The bold $\mathbf{v}_i$ indicates velocity which is a vector.
- The average velocity of the system at rest is zero.
- Recall that speed is a scalar and has magnitude only.
- The average molecular speed is not zero.
- A density is any quantity per unit volume.
    - Mass density, ρ, is mass per unit volume.
    - Number density, n, is number per unit volume.
        - Consider N molecules of mass m in volume V:

$$n = \frac{N}{V} \quad \text{and} \quad \rho = nm$$

    - Energy density is energy per unit volume (and has units of pressure).
- What is the relationship between kinetic energy of molecules and the pressure of a gas?

- Consider a perfect gas contained in a cubical box of length l.
- Define a cartesian coordinate system with axes normal to the walls (and parallel to the sides) of the cube.
- The walls of the cube reflect molecules elastically.
  - If a molecule with velocity $\mathbf{v}$ and components v_x, v_y, v_z strikes a wall of the box, then the sign of the appropriate velocity component is reversed.
  - Therefore the velocity at some later time is described by $\pm v_x, \pm v_y, \pm v_z$.
- Consider motion in the z direction.
  - S is the face of the box perpendicular to z and has the area l^2.
- In the time between two collisions with S, the molecule must move $2l$ (to the other end of the box and back).

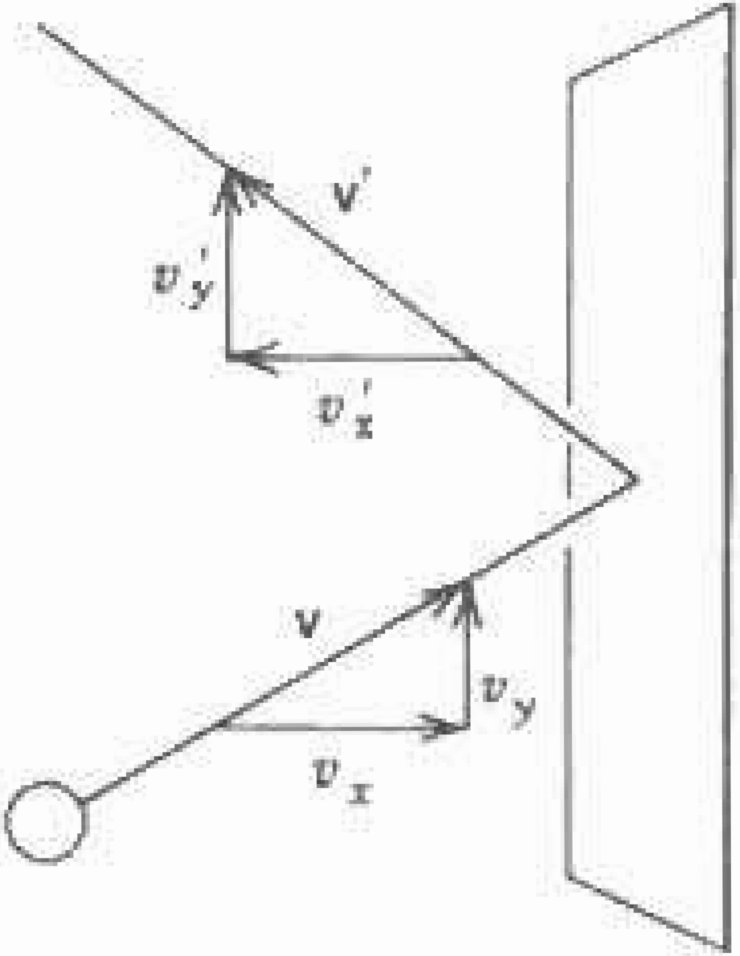


Figure 12.1 Elastic reflection of a particle from the wall of a box. The initial velocity is $\mathbf{v}$, with components v_x perpendicular to the wall and v_y parallel to the wall. After reflection the velocity is $\mathbf{v}'$, with components $v'_x = -v_x$ and $v'_y = v_y$.

- The velocity component perpendicular to S is v_z
- Therefore the time between collisions with S is $2l/v_z$
  - The frequency of collisions is $v_z/2l$
- When the molecule collides with S, its momentum changes from $+mv_z$ to $-mv_z$.
  - An equal and opposite momentum is transferred to the wall of the container.
- The total change in the z component of the momentum of a single molecule per unit time is:

$$\left[\frac{d(mv_z)}{dt}\right] = 2mv_z \cdot \frac{v_z}{2l} = \frac{mv_z^2}{l}$$

- Assume the simplest possible velocity distribution with all molecules having the same velocity components, $\pm v_x, \pm v_y, \pm v_z$.

- There are N molecules in the volume $V = l^3$
    - Therefore the total change in momentum per unit time arising from all collisions with S is:

$$\left[\sum_{i=1}^{N} \frac{d(mv_z)}{dt}\right] = \frac{Nmv_z^2}{l} = \frac{nVmv_z^2}{l} = nml^2v_z^2$$

(Recall that n is number density.)

- Pressure is defined as force per unit area.
- Force is defined as the change in momentum per unit time.
- p is the pressure of the gas
    - pl^2 is the total force on S and

$$pl^2 = nml^2v_z^2 \text{or } p = nmv_z^2$$

- The pressure of a gas is the same in all directions. Thus:

$$v_x^2 = v_y^2 = v_z^2 = \frac{1}{3}(v_x^2 + v_y^2 + v_z^2) = \frac{1}{3}v^2$$

  where v is the common speed of the molecules.
- This gives:

$$p = \frac{1}{3}nmv^2$$

- Since the kinetic energy of a single molecule is $mv^2/2$ and n is the number density of molecules, the pressure is $2/3$ of the kinetic energy density.

The Perfect Gas

- What is the relationship between pressure and energy?
- The previous treatment is restrictive.

- Not all collisions with the wall are elastic.
- Molecular speeds are not all the same.
- Directions of motion are random.
- The container is not a cube.
- It may be useful to have a more general derivation of the relationship between the distribution of velocities and the pressure and energy of a gas.
  - In most cases the generalized distribution does not need to be known, but only some of its properties.
- Consider a perfect gas in equilibrium with N molecules in volume V.
  - The molecules will move with different velocities.
- Let $f(\mathbf{v})d\mathbf{v}$ be the number of molecules per unit volume with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$.

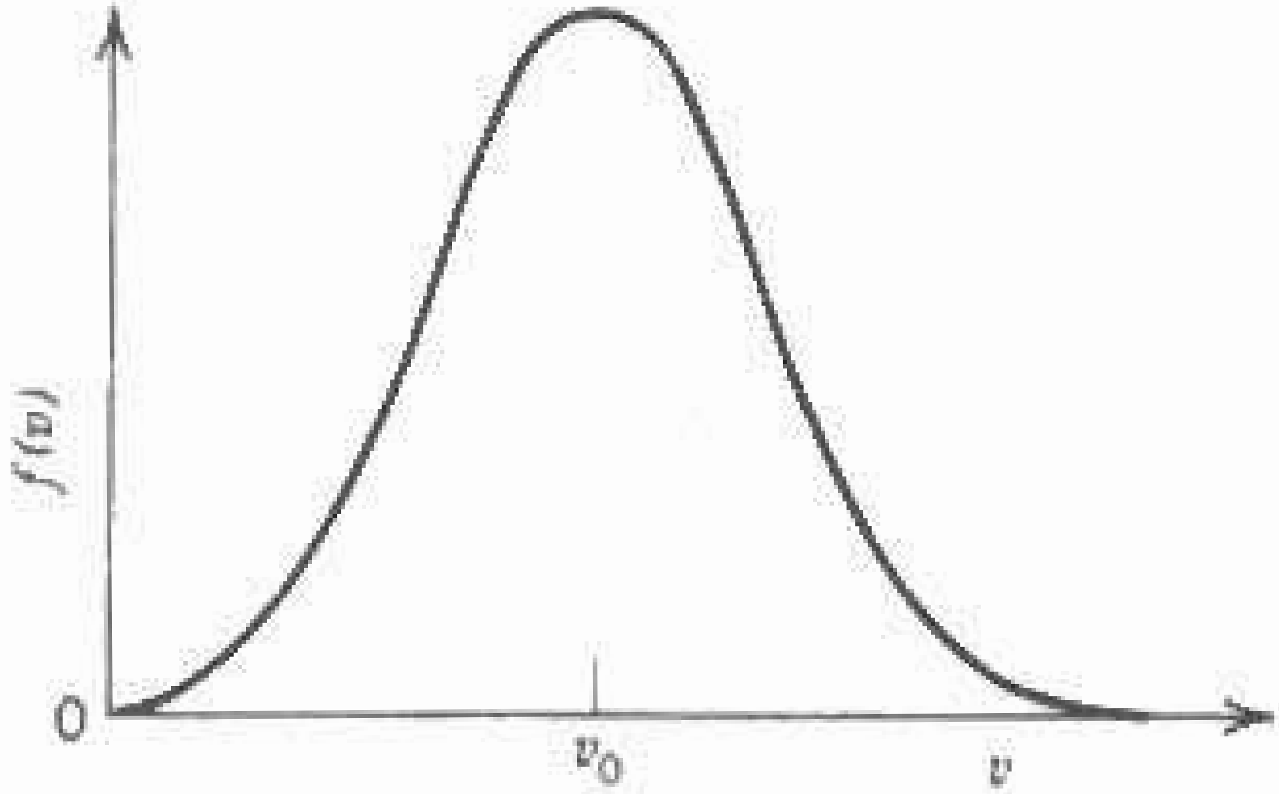
- $f(\mathbf{v})$ is the velocity distribution function.
- The total kinetic energy of all N molecules is finite. Therefore $f(\mathbf{v}) \rightarrow 0$ as $\mathbf{v} \rightarrow \infty$
- If the sum of $f(\mathbf{v})d\mathbf{v}$ is taken over all possible velocities then n, the total number of molecules per unit volume is obtained.
- This may be written as:

$$\int_{\mathbf{v}} f(\mathbf{v})d\mathbf{v} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(\mathbf{v})dv_x dv_y dv_z = n$$

- Molecular motion at equilibrium is isotropic.
    - Equal numbers of molecules in any given speed interval must travel in any direction.
    - $f(\mathbf{v})$ is independent of direction.
    - $f(\mathbf{v})$ is a function only of its magnitude, the speed v.

- Therefore, a distribution function in terms of v would be convenient.
- Consider $f(v)dv$ as the number of molecules per unit volume with speeds between v and $v + dv$.
- Consider the molecular velocity as a point in velocity space defined velocity coordinates, v_x, v_y, v_z
  - The volume element is $d\mathbf{v} = dv_x dv_y dv_z$
- But now the distribution is to be considered in terms of speed, not velocity.
  - What is the relationship between dv and $d\mathbf{v}$?
  - The molecules with the speed between v and $v + dv$ occupy a spherical shell of radius v and thickness dv.
  - The volume of this spherical shell is $4\pi v^2 dv$
- Therefore:

$$f(v) = 4\pi v^2 f(\mathbf{v})$$



igure 12.2 The distribution of molecular speeds, $f(v)$. The speed v_0, which is the most probable, is the *mode* of the distribution.

- An important property of $f(v)$:
  - At equilibrium the gas is homogenous, therefore $f(v)$ is independent of the position within the gas.
  - This is true for real molecules if the energy of interaction is independent of velocity.
- What is the internal energy of a gas arising from molecular motion?
  - A molecule of mass m and speed v has kinetic energy of $mv^2/2$.
  - The total number of molecules with speed between v and $v + dv$ is given by $f(v)dv$.
  - Contributions from all values of v are summed.

- The total internal energy U is:

$$U = \int_V \int_{v=0}^{\infty} \frac{mv^2}{2} f(v)\, dv\, dV$$

  - Since $f(v)$ does not depend on the position, it is independent of the volume, therefore the integral over volume can be separated from the integral over speed:

$$U = \int_V dV \int_{v=0}^{\infty} \frac{mv^2}{2} f(v)\, dv$$

$$U = \frac{mV}{2} \int_{v=0}^{\infty} v^2 f(v)\, dv$$

- Note that this expression may break down for real gases.

- For polyatomic molecules, there are contributions to the internal energy from the motions within the molecules.
- Real molecules can have interactions between them which will also make a contribution to the internal energy.
- What is the relationship between internal energy and pressure?
  - Pressure has been defined as force exerted by the gas per unit area of the wall of the container, i.e. the rate at which momentum is transferred to the wall.
- But the gas is homogeneous and isotropic.
  - Therefore the pressure must be the same anywhere in the gas.
- Consider a plane surface S anywhere within the gas.

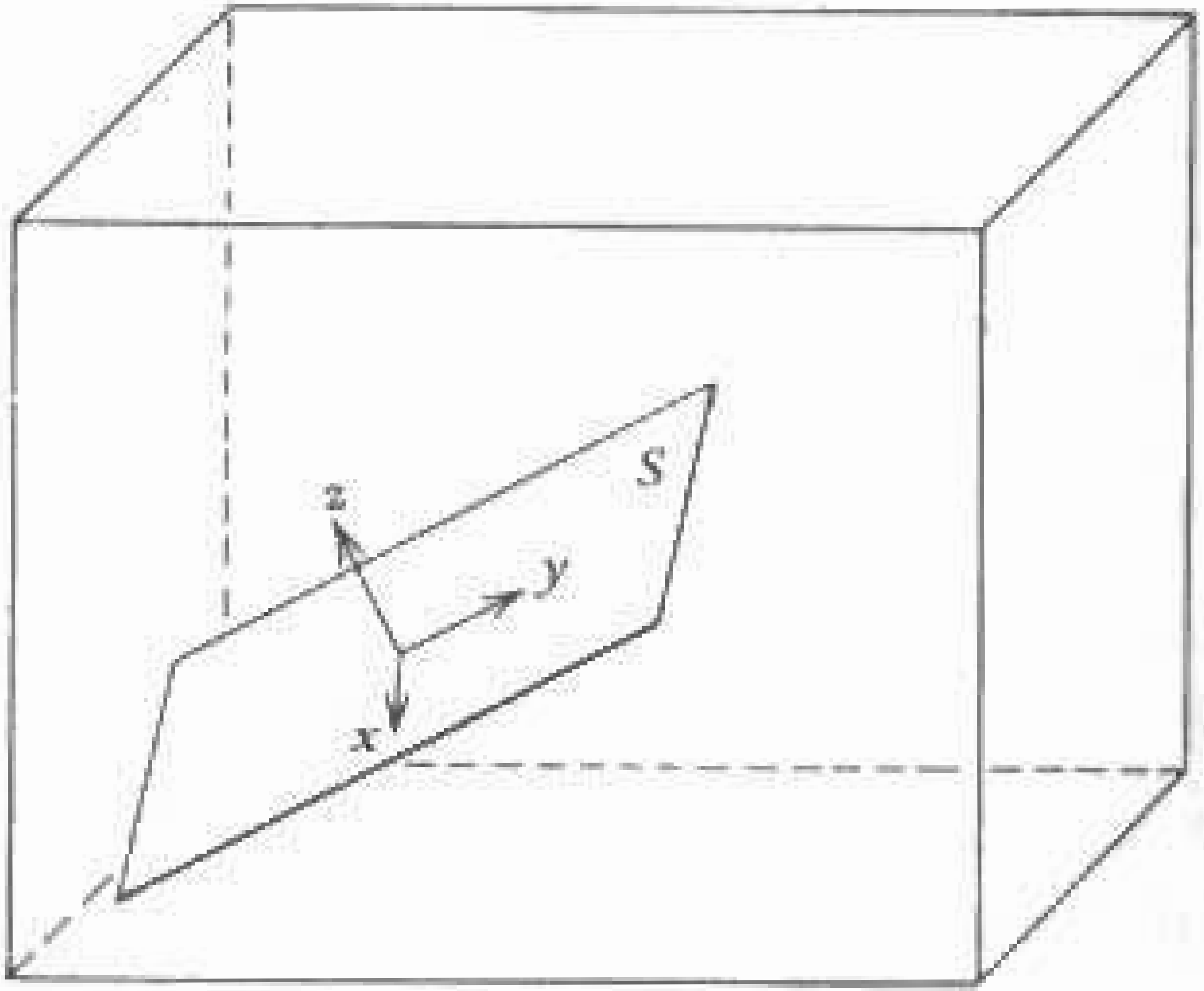
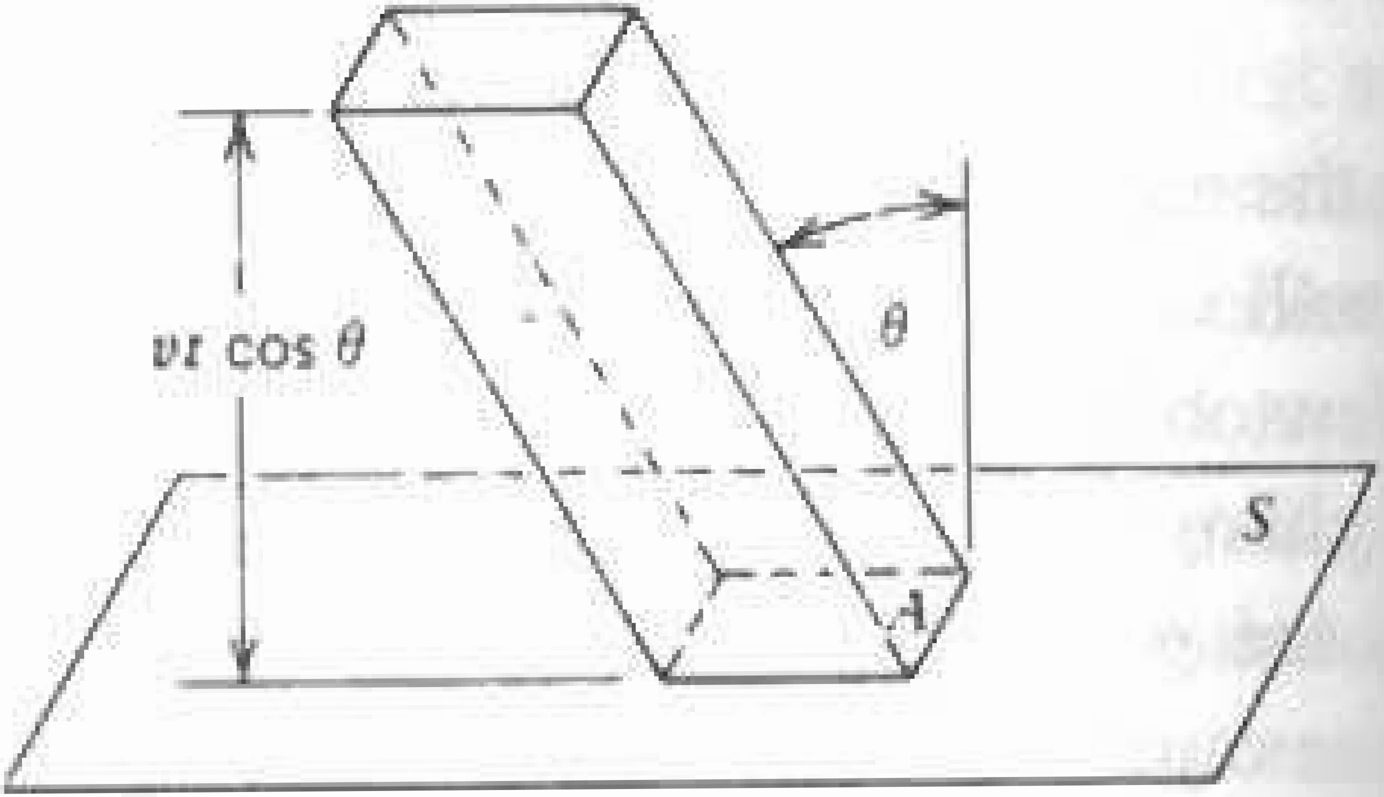


Figure 12.3 The plane surface *S* is fixed at an arbitrary position in a container of gas. The *xyz* coordinate system is defined so that the *z* axis is normal to *S*.

- Molecules hit this surface in the same way as they hit the walls.
- When a molecule with mv_z as the z component hits the surface, momentum $2mv_z$ is transferred to S.
- The pressure on S is total momentum transmitted per unit time and per unit area of S.
- The pressure is the same on both sides of S when the system is at equilibrium.
- Now replace S with an imaginary plane in the same position.
  - The molecules will cross this imaginary plane with momentum mv_z.
  - **By definition**, pressure is same whether the wall is there or not.

- Thus the pressure normal to the imaginary plane S is twice the momentum transported from one side across S per unit time and per unit area.
- What is the rate of momentum transfer?
  - Consider those molecules crossing S in the positive z direction.
  - θ is the angle between the molecule's trajectory and S.
- $F(\theta, v) d\theta dv$ is the number of molecules with speed between v and $v + dv$ that cross S per unit time and per unit area at angles between θ and $\theta + d\theta$.
- Each molecule has momentum mv with z component $mv \cos \theta$.
  - Only the z component contributes to the pressure.



igure 12.4 All the molecules within the inclined prism that have elocity **v** in the direction θ will strike the area A within time t. The olume of the prism is $A\,vt\cos\theta$.

- The contribution of the other components of the motion cancel out due to the isotropy of the gas and make no net contribution to the pressure.
- Therefore the contribution to the pressure from the molecules in the range $dvd\theta$ is the number per unit time per units area multiplied by twice the z component of the momentum transported per molecule.

$$dp = 2mv\cos\theta F(\theta, v)d\theta dv$$

- This is integrated over all possible values of θ and v that represent molecules crossing z in the positive direction to give the total pressure:

$$p = \int_{v=0}^{\infty}\int_{\theta=0}^{\pi/2} 2mv\cos\theta F(\theta, v)d\theta dv$$

- What is $F(\theta, v)$? It is the product of:
    - the number of molecules per unit volume with speed between v and $v + dv$ moving with angles between θ and $\theta + d\theta$, i.e. $f(\theta, v) d\theta dv$.
    - The volume occupied by all molecules capable of crossing S per unit time, i.e. the volume of the prism.
    - The volume of the prism (Figure 12.4) is $Avt \cos\theta$ for a base of area A and time t, thus per unit area and per unit time, this becomes $v \cos\theta$

$$F(\theta, v) d\theta dv = v \cos\theta \; f(\theta, v) d\theta dv$$

    - Recall that $f(v) dv$ is the total number of molecules per unit volume with speeds between v and $v + dv$.

- Thus:

$$\int_\theta f(\theta, v)d\theta dv = f(v)dv$$

- Recall also that molecular motion is isotropic. Therefore the integration is over the range of solid angles between θ and $\theta + d\theta$.
    - Note also that $f(\theta, v)d\theta dv$ and $f(v)dv$ are in the same relationship as are the solid angles between $\theta + d\theta$ and 4π.
        - The solid angle between θ and $\theta + d\theta$ is $2\pi \sin\theta d\theta$
        - Therefore:

$$\frac{f(\theta, v)d\theta dv}{f(v)dv} = \frac{2\pi \sin\theta d\theta}{4\pi} = \frac{1}{2} sin\theta d\theta$$

- Thus the pressure is:

$$p = \int_{v=0}^{\infty} \int_{\theta=0}^{\pi/2} (2mv\cos\theta)(v\cos\theta)\left(\frac{1}{2}\sin\theta d\theta\right) f(v)dv$$

$$p = m\int_{v=0}^{\infty} v^2 f(v)dv \int_{\theta=0}^{\pi/2} \cos^2\theta \sin\theta d\theta$$

- The angular integral is of the form:

$$\int u^2 du = \frac{u^3}{3} + C$$

where $u = \cos\theta$ and $du = -\sin\theta d\theta$

- Therefore

$$\int_{\theta=0}^{\pi/2} \cos^2\theta \sin\theta d\theta = -\frac{1}{3}\left(\cos^3(\pi/2) - \cos^3(0)\right)$$

$$= -\frac{1}{3}(0 - (1)^3) = \frac{1}{3}$$

- Therefore:

$$p = \frac{m}{3}\int_0^\infty v^2 f(v) dv$$

- Recall that:

$$U = \int_V \int_{v=0}^\infty \frac{mv^2}{2} f(v)\ dv\ dV$$

thus

$$p = \frac{2}{3}\frac{U}{V}$$

which is consistent with

$$p = \frac{1}{3}nmv^2$$