1 Empirical Properties of Gases

system — A thermodynamic system is that part of the physical universe the properties of which are under investigation. The system is confined to a definite place in space by the ***boundary*** which separates it from the rest of the universe, the ***surroundings***.

properties — The properties of a system are those physical attributes that are perceived by the senses, or are made perceptible by certain experimental methods of investigation.

state of a system — A system is in a definite state when each of its properties has a definite value.

equation of state of the system — the mathematical relationship between the values of the properties : mass, volume, temperature, and pressure.

pressure — Force divided by the area to which the force is applied.

EXAMPLE:

Find the pressure at the base of a column of liquid of mass density ρ (rho) and height h at the surface of the earth.

Start with Definitions: p = Force/Area
density = mass/volume

Solution: Volume of the column of liquid = Ah
mass = ρAh
gravitational force = mg
Force = ρAhg
pressure = ρhg *This is the equation you need.*

760 mm mercury at 298.15 K therefore exerts a pressure equal to:

$$13.59 \text{ g cm}^{-3} \times (10^{2} \text{ cm/m})^{3} \times (10^{-3} \text{ kg/g})$$
$$\times\, 760 \text{ mm} \times (10^{-3} \text{ m/mm})$$
$$\times\, 9.81 \text{ m s}^{-2}$$
$$= 1.01325 \times 10^{5} \text{ kg m}^{-1} \text{ s}^{-2}$$

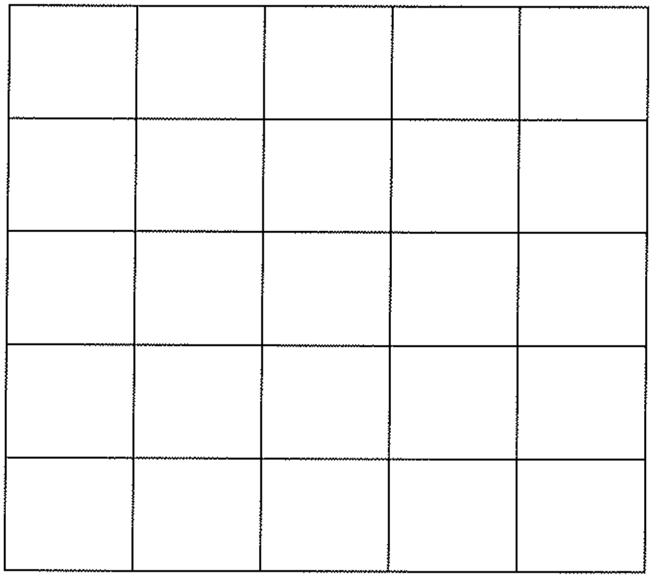
$$1 \text{ Pa} \equiv 1 \text{ kg m-}^{1} \text{ s}^{-2}$$

temperature — a property of a system

When two objects at different temperatures are placed and left in contact with each other, a change in physical state can occur. Later on we will see that the change in state can be interpreted as arising from a flow of energy in the form of heat, from one object to the other. The ***temperature*** is the property that tells us the direction of the flow of energy. If energy flows from object A to object B when they are in contact, then we say that A has a higher temperature than B. When two objects at different temperatures are placed and left in contact with each other, their temperatures eventually become equal. We say that the objects are then in ***thermal equilibrium*** with each other.

A wall between the two objects is ***diathermic*** if a change of state is observed when two objects are brought into contact.

extensive variable (extensive property) — a property whose value can be obtained by summing the values of that property in every part of the system



examples: n V

intensive variable (intensive property) — a property whose value is not obtained by such a process of summation but is measured at any point in the system, and it has a uniform value throughout the system at equilibrium.

examples: T p

1.1 The Ideal Gas

One experimental information that is very useful is that at a given pressure and temperature, the molar volume *V/n* of a gas is approximately the same regardless of the identity of the gas.

Avogadro's principle — Equal volumes of gases at the same pressure and temperature contain the same numbers of molecules.

The volume of a fixed amount of a gas at a fixed low pressure is found to vary with temperature in a straight line and has the same temperature intercept (***-273.15*** on the Celsius scale) regardless of the gas or the pressure (only that *p* is low enough)
This behavior defines a temperature scale called ***absolute temperature***, in which one Kelvin is the same temperature increment as one Celsius and the offset is -273.15.

$$T\ (\mathrm{K}) = t\ (^\circ\mathrm{C}) + 273.15$$

Within a narrow range of temperature and pressure values, some gases approximately obey a simple equation of state:

Perfect Gas Equation or
Ideal Gas Equation of State

$$pV = nRT$$

In the limit of $p \to 0$, all empirical gas behavior approach the ideal gas equation of state. $pV_m = RT$ *where* V_m = *molar volume*

gas constant — R

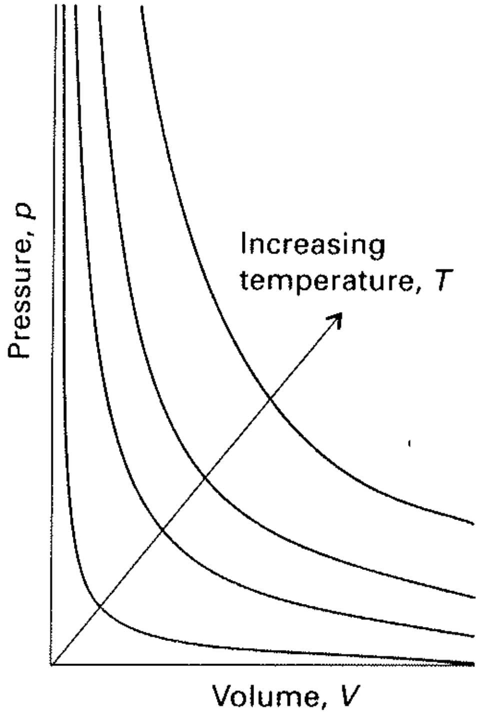
8.20578×10^{-2} L atm K^{-1} mol^{-1}
8.31451×10^{-2} L bar K^{-1} mol^{-1}
8.31451 Pa m^3 K^{-1} mol^{-1}

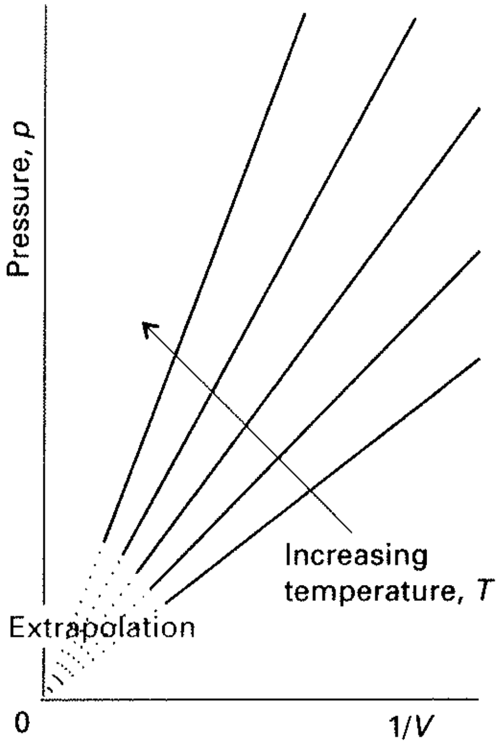
8.31451 J K^{-1} mol^{-1}
1.98722 cal K^{-1} mol^{-1}

In each of the pVT (or Z) diagrams that follow, every point represents a state of the system.

isotherm — a mathematical curve that corresponds to a relation between a set of (2 or more) variables at constant temperature.

Isotherms for an ideal gas:



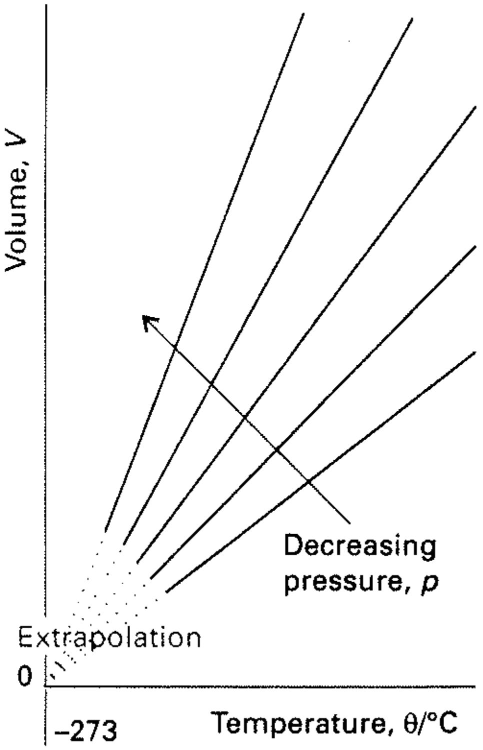


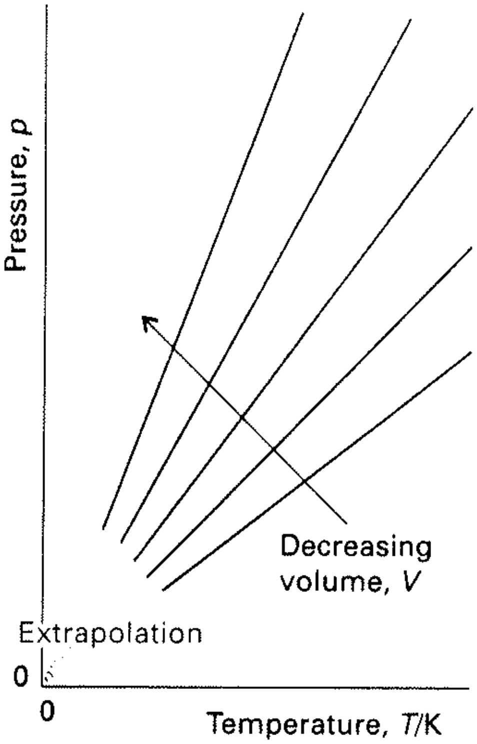
isobar — a mathematical curve that corresponds to a relation between a set of (2 or more) variables at constant pressure.

isochore — a mathematical curve that corresponds to a relation between a set of (2 or more) variables at constant volume.

isobars
for a fixed amount
of an ideal gas
All extrapolate to zero
V at -273.15°C

isochores
for a fixed amount
of an ideal gas
Extrapolate to zero
p at -273.15°C





The Barometric Distribution Law:

EXAMPLE:

What is the influence of the gravity field? Devise a quantitative answer.

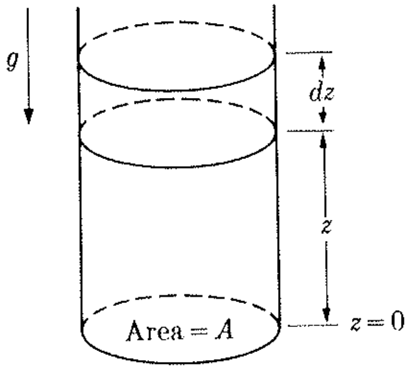
The pressure of the gas has the same value everywhere in the container, in all the discussions of properties of gases in your textbook. ***This assumption is correct only in the absence of force fields.*** All measurements are done on laboratory systems, which are always in the presence of a gravitational field.

What is the influence of the gravity field?

For gaseous systems of ordinary size: so slight as to be imperceptible.

For liquids: quite pronounced; the pressure will be different at different vertical positions in a container.

Draw a Picture:



Column of gas in a gravity field.

Principles and Definitions involved:

Pressure at any height z in the column is determined by the total weight of fluid in the column above that height.

Weight = Force = $F = mg$,

Pressure = force per unit area: $p = F/A$

Solution:

$F_z \equiv$ weight of fluid in the column above height z

$F_{z+\mathrm{d}z} \equiv$ weight of fluid in the column above height $z+\mathrm{d}z$

$dF \equiv$ weight of fluid in the column between heights z and $z+\mathrm{d}z$

$F_{z+\mathrm{d}z} + \mathrm{d}F = F_z$

If rho ρ = density of the fluid at height z, then the mass of fluid in the column between heights z and $z+\mathrm{d}z$ is $\rho A\mathrm{d}z$.

$$\mathrm{d}F = (\rho A\mathrm{d}z)g \qquad (1)$$

Now relate this to pressure:

p is the pressure at height z $\quad F_z = pA$

$p+\mathrm{d}p$ = pressure at height $z+\mathrm{d}z$ $\quad F_{z+\mathrm{d}z} = (p+\mathrm{d}p)A$

$\therefore\ A\mathrm{d}p + \mathrm{d}F = 0$ (2)

Combining eq. (1) and (2),

$\mathrm{d}p = -\rho g\mathrm{d}z.$

Now, all we have to do is integrate.

For an incompressible liquid , the density is independent of pressure:

$$\int_{p0}^{p} \mathrm{d}p = - \int_{0}^{z} \rho g\mathrm{d}z$$

Answer: $p - p_0 = -\rho gz$ where p_0 is the pressure at height $z = 0$.

{of great interest to deep-sea divers}

For a gas, ρ depends on pressure.

Ideal gas: $pV = nRT$ or $pV = (m/M)RT$

density $= \rho = (m/V) = (M/RT)p$,

to be substituted into

$\mathrm{d}p = -\rho g\mathrm{d}z$ giving,

$\mathrm{d}p = -(M/RT)pg\mathrm{d}z$

$\mathrm{d}p/p = -(M/RT)g\mathrm{d}z$ *for an ideal gas*

$$\int_{p0}^{p} \mathrm{d}p/p = - \int_{0}^{z} (M/RT)g\mathrm{d}z$$

$ln(p/p_0) = - (M/RT)gz$ or

$(p/p_0) = \exp[- (M/RT)gz]$

the barometric formula
(as given in # 1.35 in p. 43 of textbook.)

Mixtures of Gases

composition variables:

molar concentration $c_i = n_i / V$

mole fraction $x_i = n_i / (n_1 + n_2 + n_3 + \ldots)$

$$= n_i / \sum_i n_i$$

$$\sum_i x_i = 1$$

partial pressure of a gas in a mixture of gases — $p_i \equiv x_i p$

By this definition, it follows that

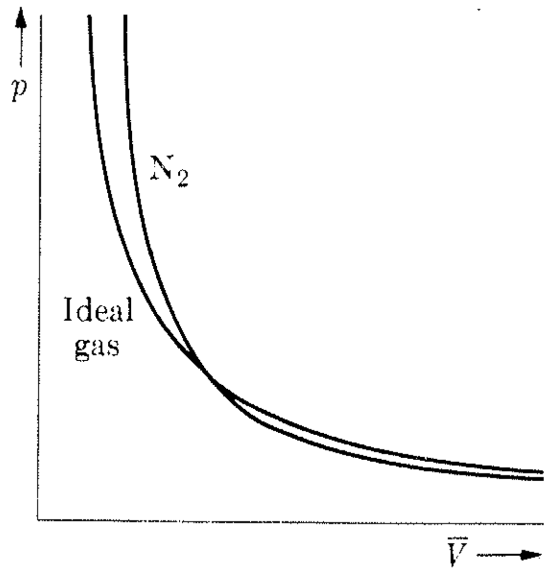
$p_1 + p_2 + p_3 + \ldots = \sum_i x_i\, p = p$

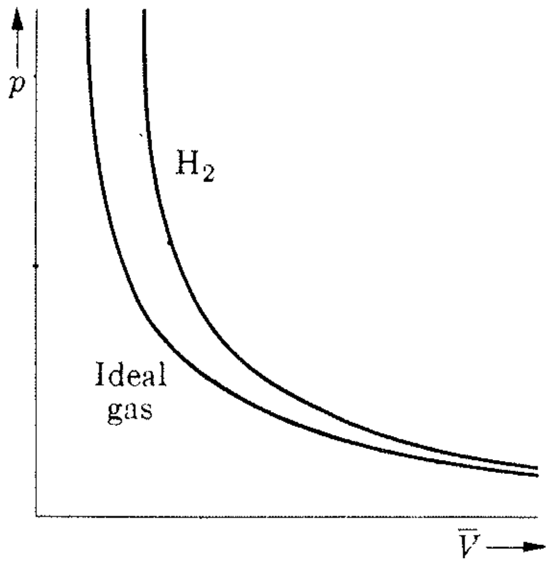
Dalton's Law: At any specified temperature the total pressure exerted by a gas mixture is equal to the sum of the partial pressures of the constituent gases. By defining partial pressure as $p_i \equiv x_i p$, this statement is true for all gases, not just ideal mixtures. The partial pressures and the total pressure have '**not necessarily simple**' relations to temperature, composition and total volume. If the gas is ideal, then the partial pressure would be the pressure the gas would exert if it were alone in the container of volume V at temperature T.

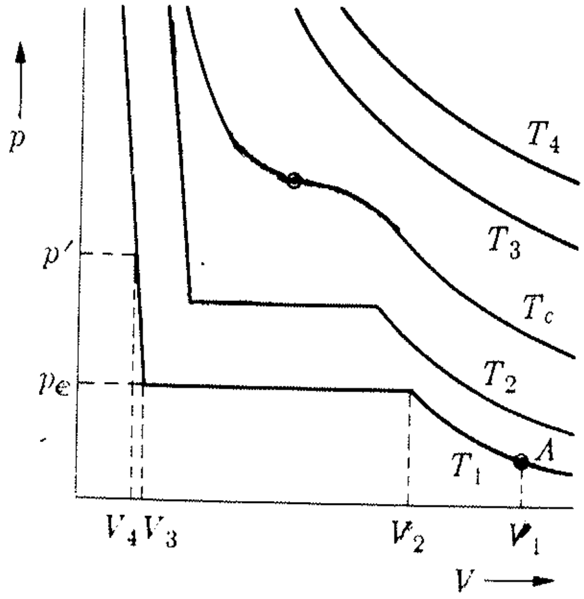
1.2 Real gases

isotherms of real gases:

the magnitude of
the deviations has been exaggerated to show the effect.



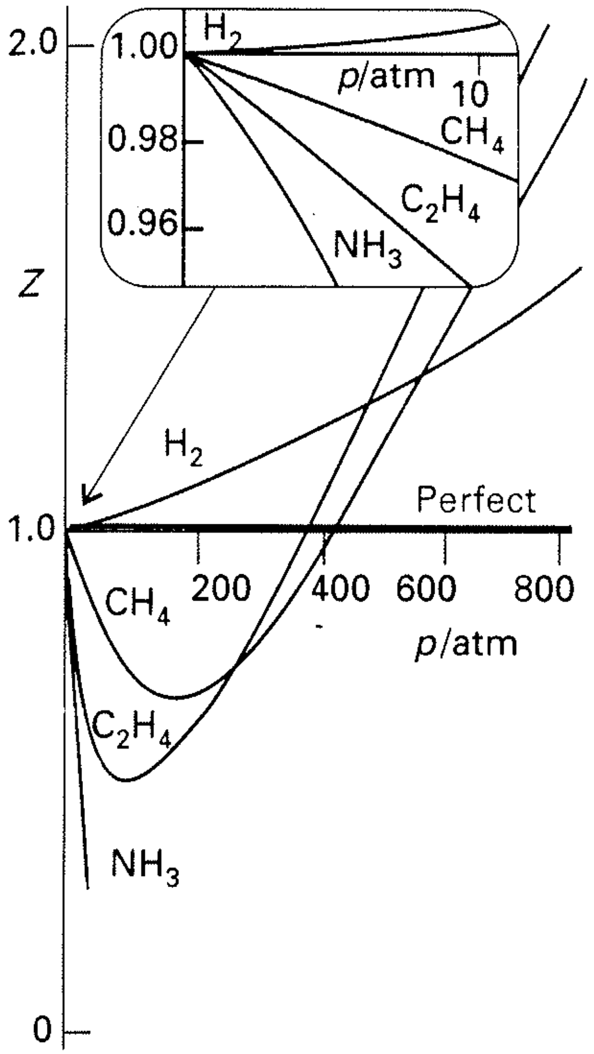




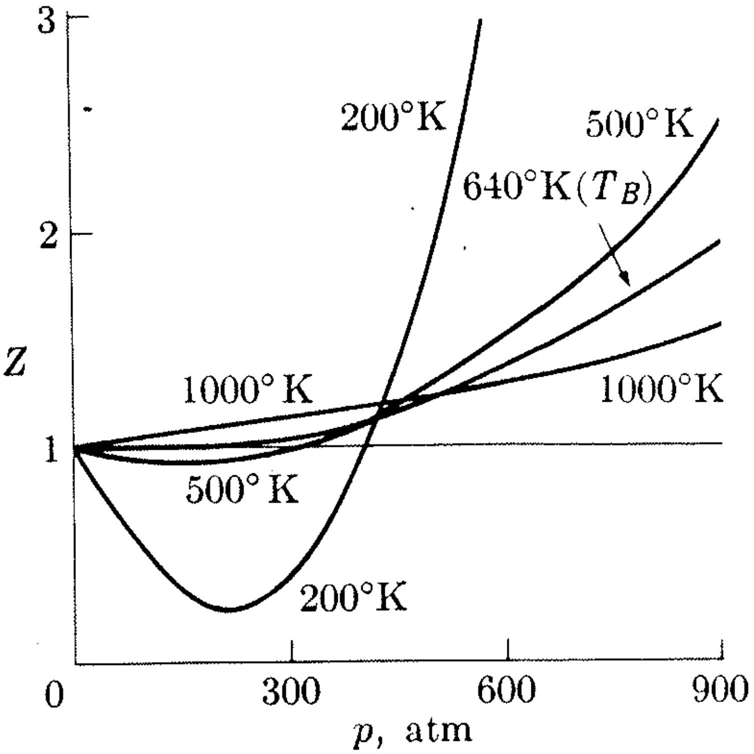
compressibility factor or ***compression factor*** — $\boldsymbol{Z \equiv pV_m/RT}$

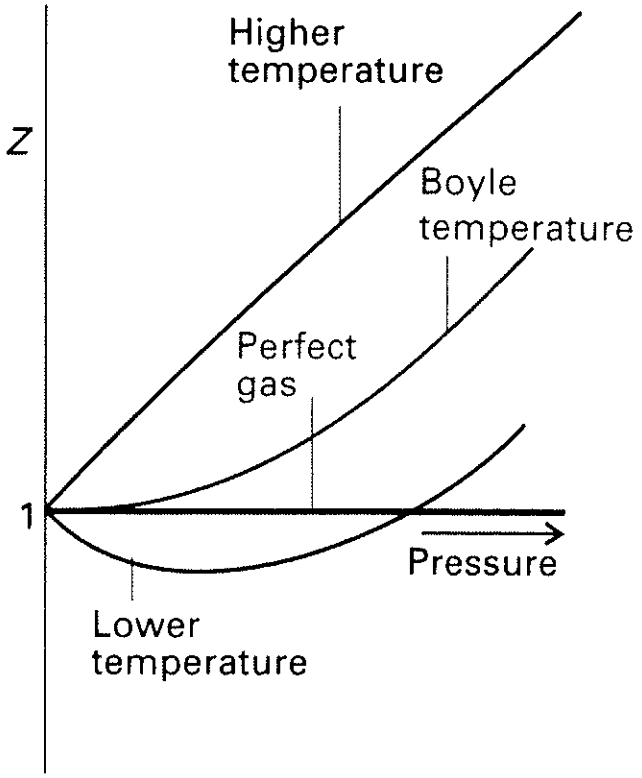
For an ideal gas, Z=1 under all conditions of T and p.

Variation of Z with p at 0°C:



Variation of Z with p for CH_4 at several temperatures:





Some equations of state:

van der Waals equation of state:

$$p = nRT/(V-nb) - n^2a/V^2$$

or $$p = RT/(V_m-b) - a/V_m^2$$

or $$Z = V_m/(V_m-b) - a/RTV_m$$

Significance of *b* and *a*:

b has units of volume/mole. It takes into account the effect of molecular size, the volume of the molecules themselves. {The empty space between the molecules extrapolate to zero as the temperature goes down as required by the ideal gas equation of state.}

a has units of $p\times(\text{concentration})^{-2}$. It takes into account the interaction between molecules which diminish the pressure that would be exerted by completely independently moving particles.

General virial equation of state:

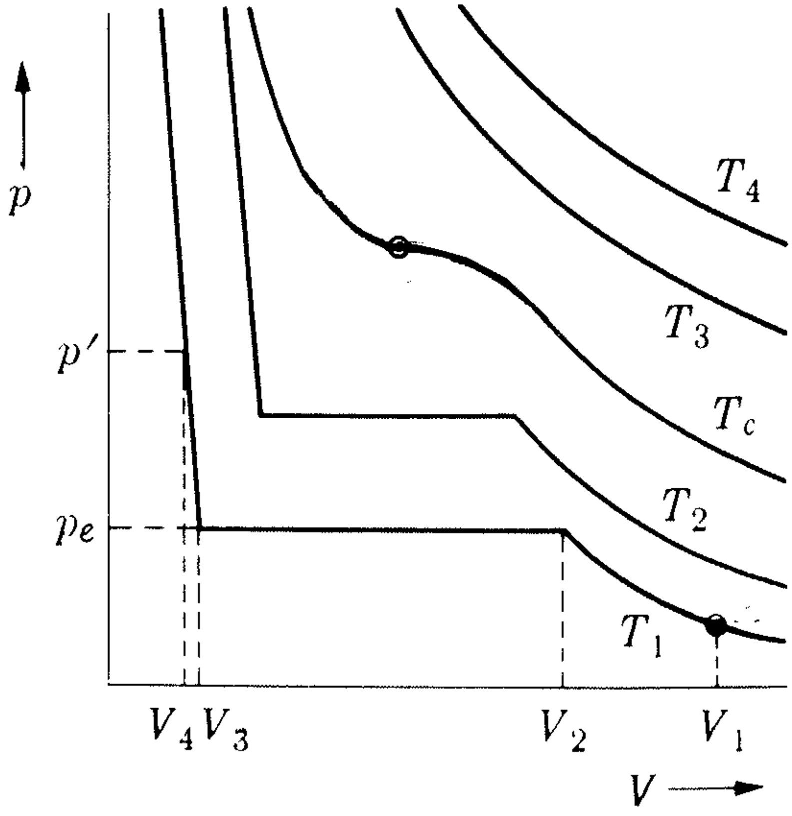
$Z = 1 + B/V_m + C/V_m^2 + D/V_m^3 + \ldots$

B, C, D,... are called the second, third, fourth, ...virial coefficients.

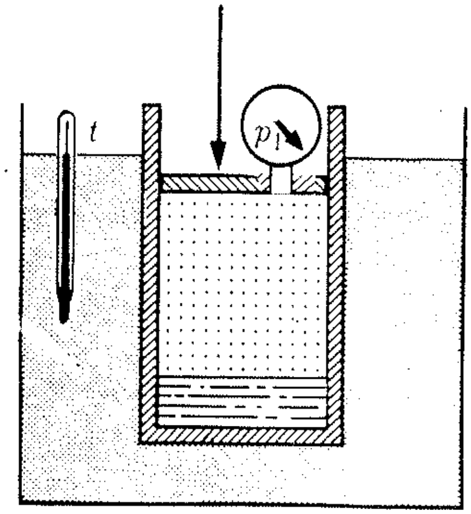
If enough terms are included, the general virial equation of state can describe any observed *p, V, T* behavior.

The Critical Temperature

Consider again the isotherms of a real gas:



Experiment



isothermal experiment at T_4 or T_3:

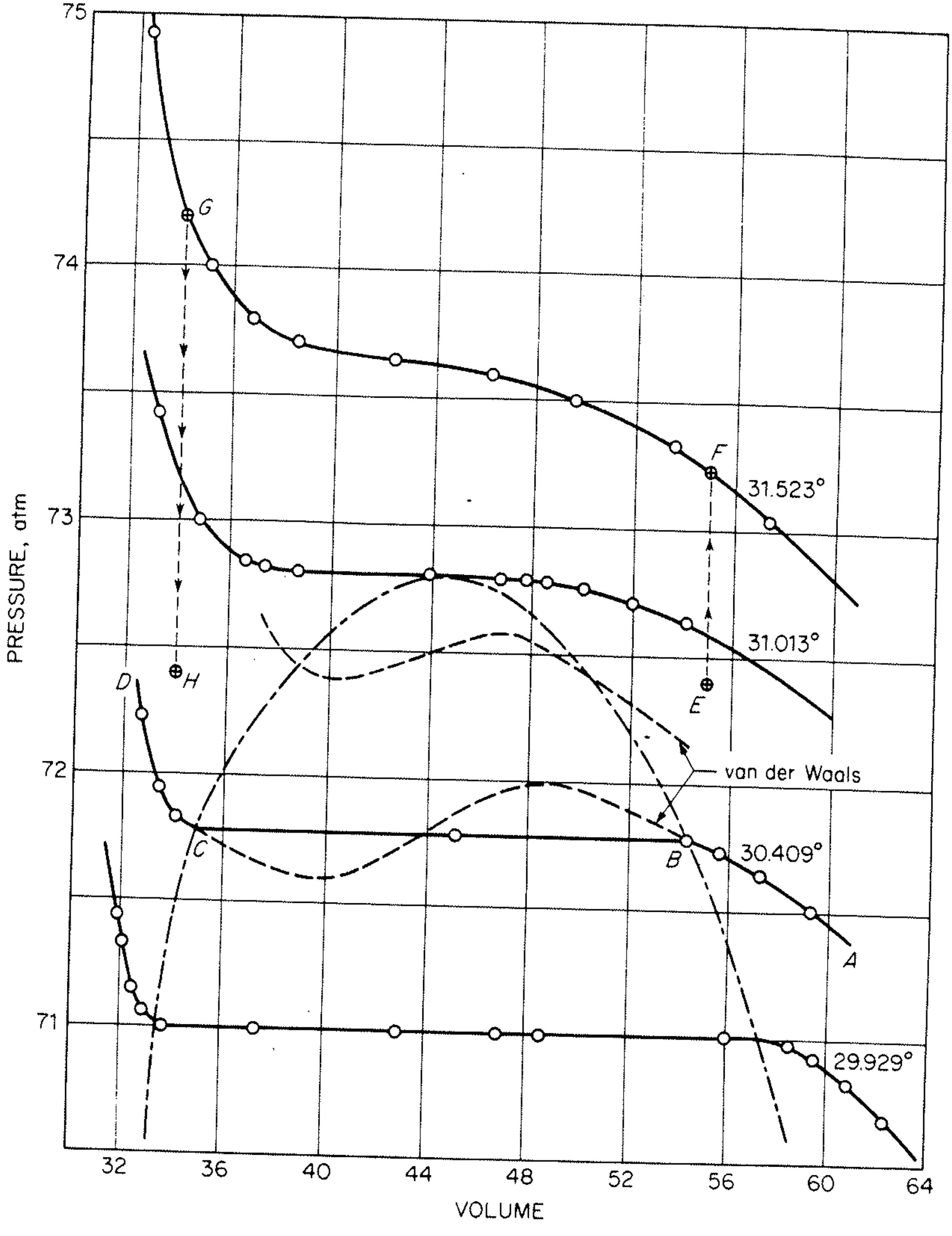
When the experiment is carried out isothermally at temperatures T_4 or T_3, reduction of the volume produces an increase in pressure reading as the system undergoes changes in state along the curves T_4 and T_3.

isothermal experiment at T_1:

When the volume is decreased from V_1 to V_2 isothermally at temperature T_1, first the pressure reading smoothly increases along the curve. Then as the first drops of liquid appear, the pressure no longer changes, while at the same time, as the volume goes down from V_2 to V_3 more and more liquid forms. At V_3 the last trace of gas disappears. Further reduction in volume compresses the liquid and the pressure reading rises steeply.

Other isothermal experiments:

In experiments at higher temperatures than T_1, a plateau in the pV curve is also observed, but a narrower plateau, until finally, the very narrow plateau reduces to *a point*, i.e., no plateau at all when the temperature of the experiment is at T_c, the ***critical temperature of the substance***.



Isotherms of carbon dioxide near the critical point.

There is a certain maximum pressure p_c (***the critical pressure***) and a certain maximum temperature T_c (***the critical temperature***) at which liquid and vapor can coexist. That is, liquid and vapor can coexist only at values below p_c and T_c , but at values above p_c and T_c , only one continuous fluid can exist.

It turns out that the values of p_c and T_c (and of course the molar volume V_{mc} can be obtained also) can be used to reduce the equations of states of all gases so that they can all be compared with one another in a reduced form of the equation of state.

reduced pressure,	$p_r \equiv p/p_c$
reduced temperature,	$T_r \equiv T/T_c$
reduced volume,	$V_r \equiv V_m/V_{mc}$

Law of Corresponding States:
Z depends only on T_r and either one of p_r or V_r.

In other words, the law of corresponding states predicts that when Z is plotted against p_r for any fixed T_r, all substances fall on the same curve!!

It is observed experimentally that the equation of states of many substances may be correlated in this way, even though more accurate measurements reveal differences.

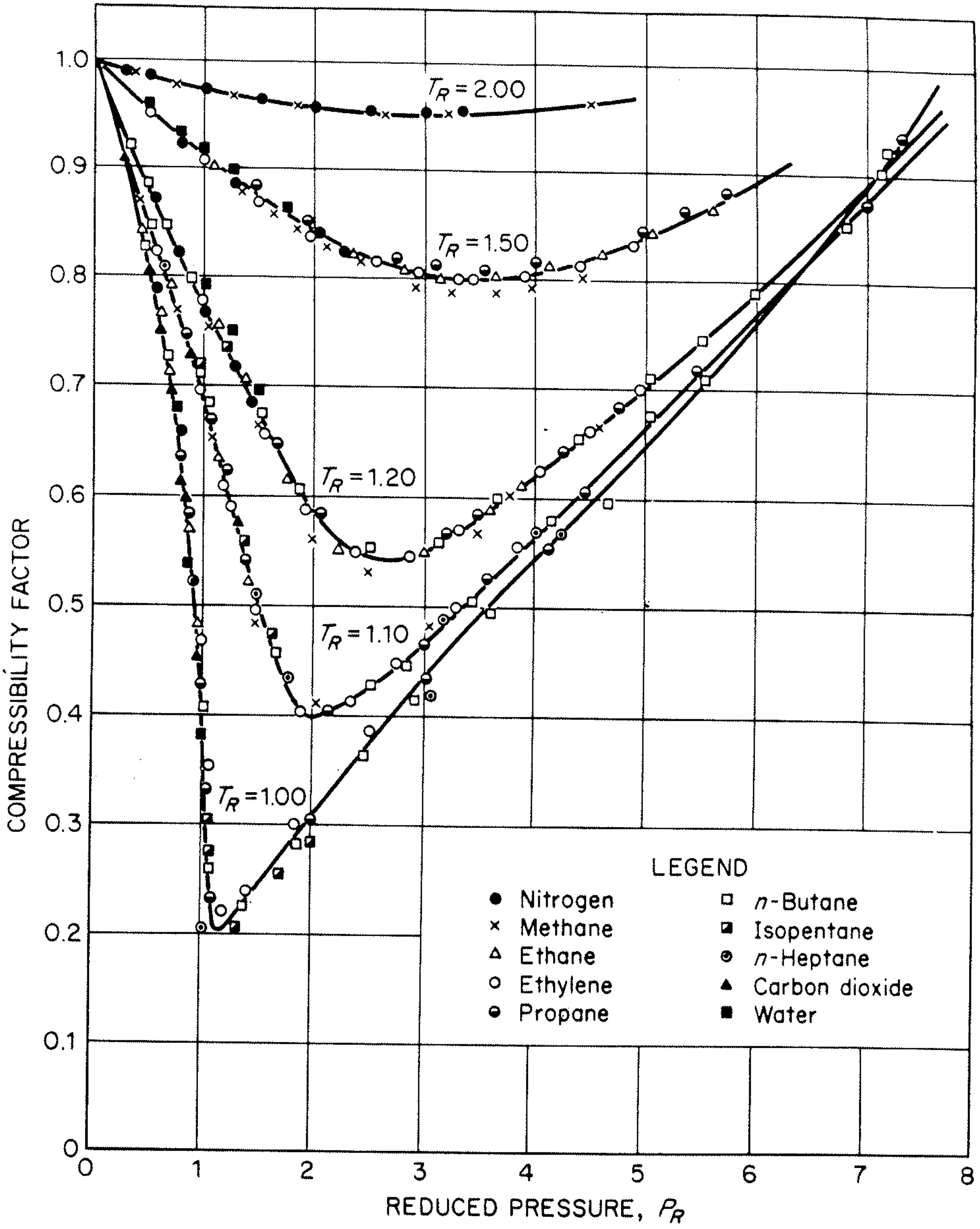


FIG. 1.8 Compressibility factor as function of reduced state variables.