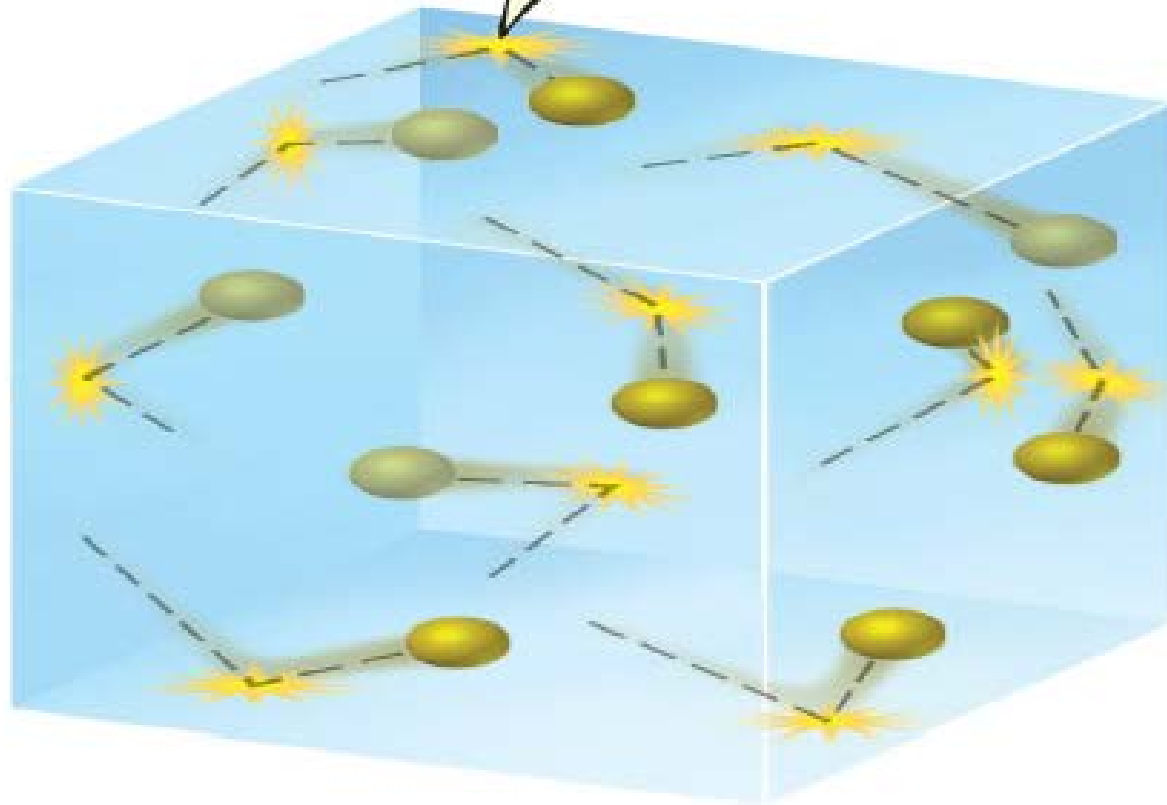# Chapter one _engineering chemistry _part2

Kinetic-Molecular Theory

Pressure inside container comes from collisions of gas molecules with container walls

Main Tenets of Kinetic-Molecular Theory

1 Gases consist of large numbers of molecules that are in continuous, random motion.

2 The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.

3 Attractive and repulsive forces between gas molecules are negligible.

4 Energy can be transferred between molecules during collisions (elastic collisions), but the average kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant.

5 The average kinetic energy of the molecules is directly proportional to the absolute temperature
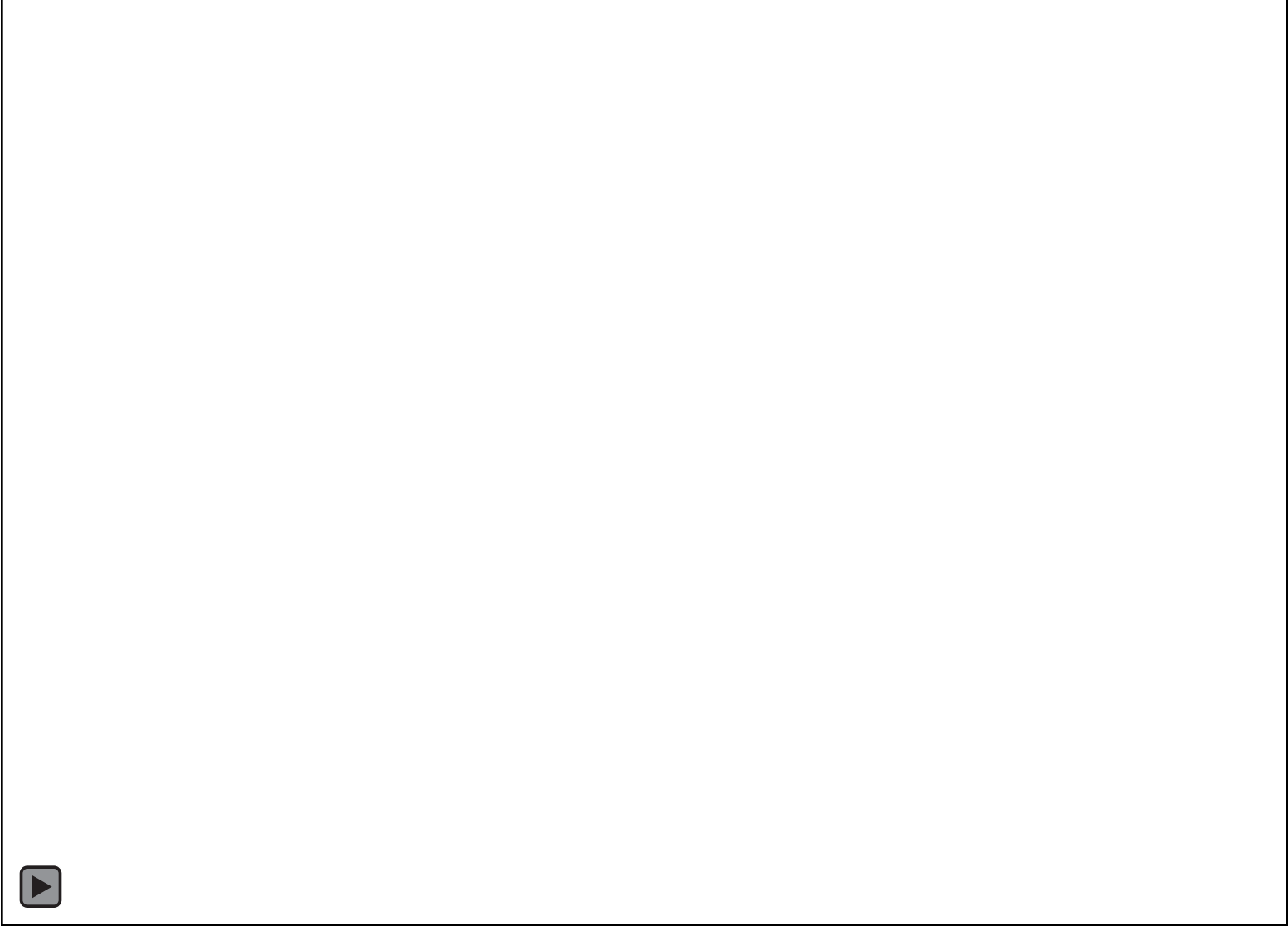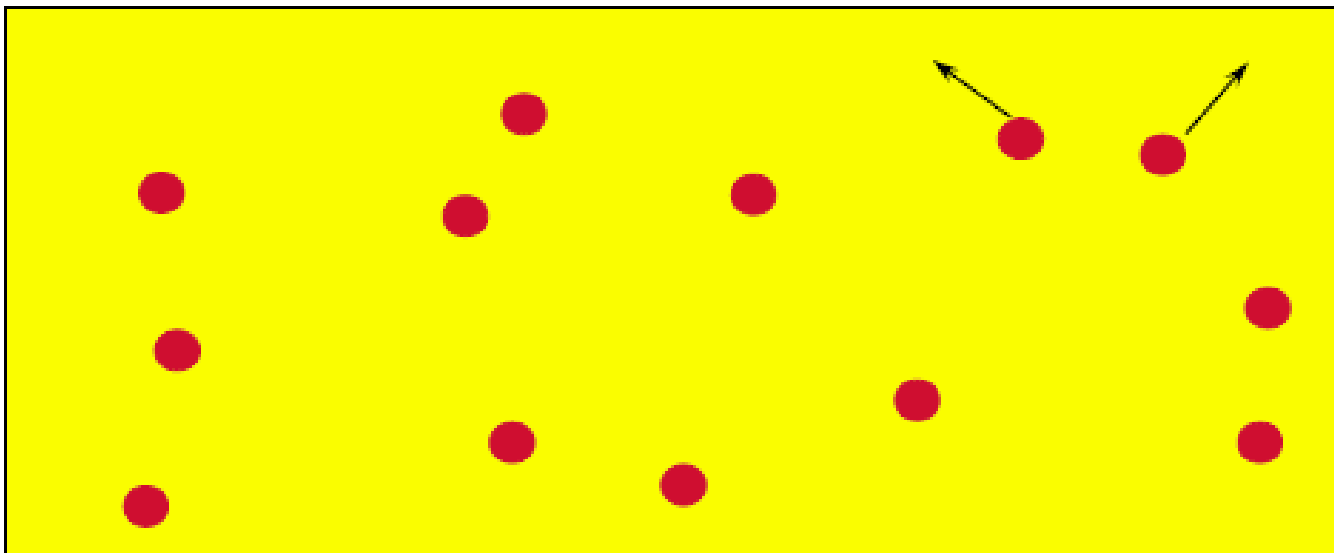
Kinetic Molecular Theory

Ideal-Gas Equation $\longrightarrow$ $PV = nRT$

- Particles in an ideal gas...
    - have no volume.
    - have elastic collisions.
    - are in constant, random, straight-line motion.
    - don't attract or repel each other.
    - have an avg. KE directly related to Kelvin temperature.

Real Gases

Ideal-Gas Equation $\longrightarrow$ $$PV = nRT$$
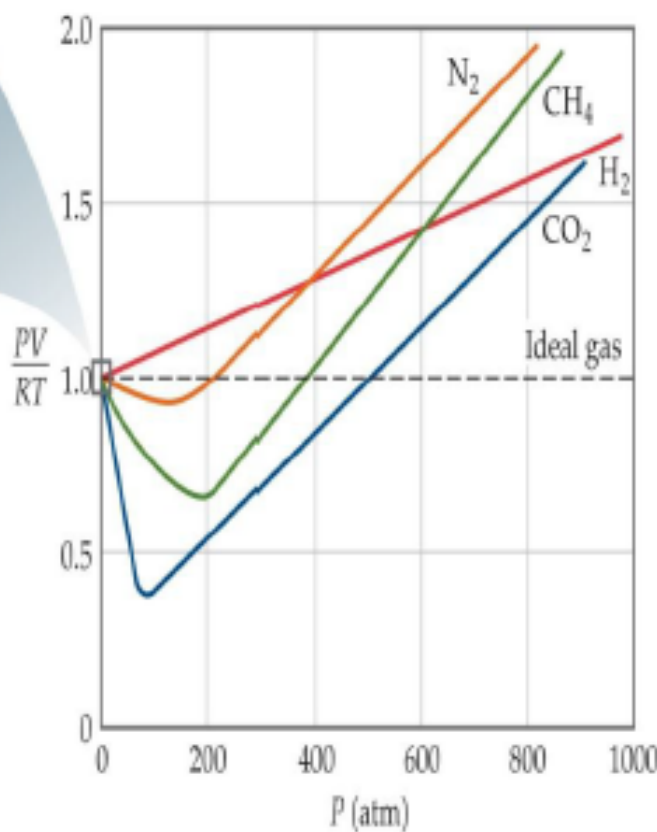
➢ In the real world, the behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.

➢ Even the same gas will show wildly different behavior under high pressure at different low temperatures.

Real Gases

$$\frac{PV}{RT} = n$$

This form of the equation tells us that for 1 mol of ideal gas, the quantity PV/RT equals 1 at all pressures.
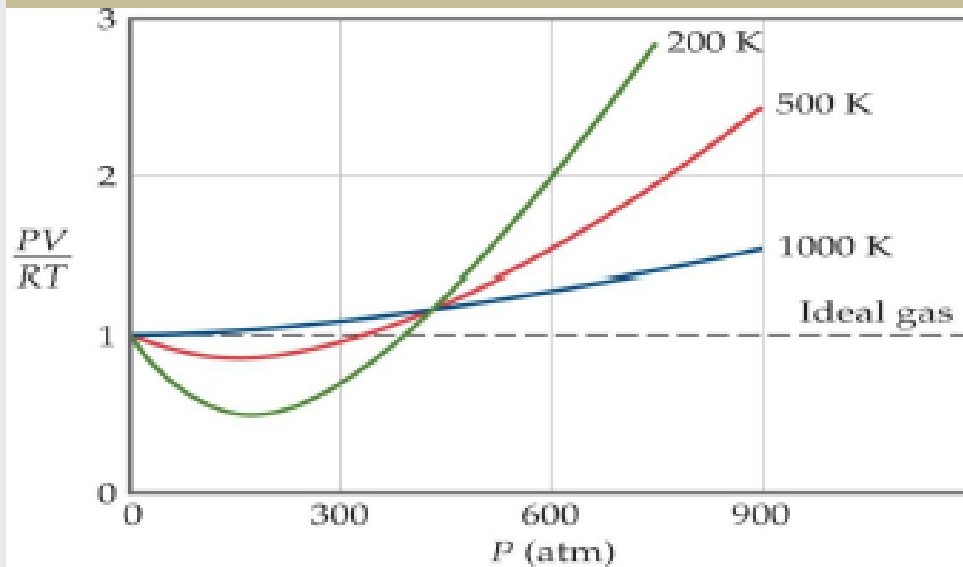

At high pressures, the deviation from ideal behavior ($PV/RT = 1$) is large and different for each gas.

Real gases, in other words, do not behave ideally at high pressure.

At lower pressures, the deviation from ideal behavior is small, and we can use the ideal-gas equation without generating serious error.

4

Real Gases

Deviation from ideal behavior also depends on temperature.
As temperature increases, the behavior of a real gas more nearly approaches that
of the ideal gas

Even the same gas will show wildly different behavior under high pressure at different low temperatures.

True or false:
Nitrogen gas behaves more like an ideal gas as the temperature increases.

In general, *the deviation from ideal behavior increases as temperature decreases.*
* The behavior of gases only conforms to the ideal gas equation at relatively high temperature and low pressure.

5

Real gases & Compressibility factor

- From the ideal gas equation: $PV = nRT$

- For 1 mole of a gas: $PV / RT = 1$

But:

- For the real gases : $PV / RT \neq 1$

- **Generally we can write:**

  - $PV / RT = Z$

Where

- **Z : compressibility factor**

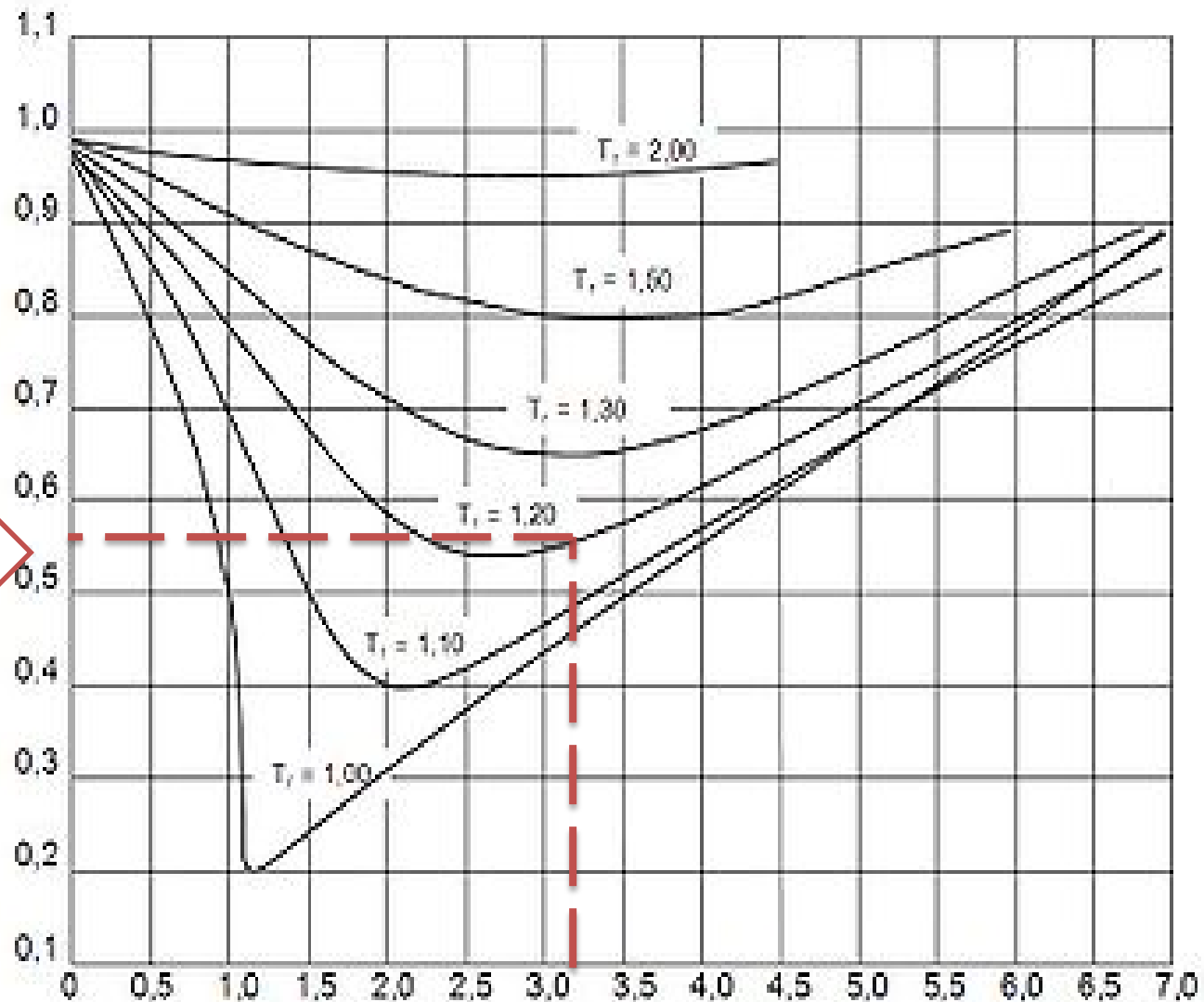# Real gases & Compressibility factor

$$PV / RT = Z$$

Where

Z : compressibility factor

- If:

- Z= 1   ideal gas behavior

- Z > 1   Real gas (positive deviation from ideal behavior)

- Z < 1   Real gas (negative deviation from ideal behavior)

$Z=PV_m/RT$

Reduced Pressure, Pr

Reduced Pressure $\qquad P_r = P/P_c$

Reduced Volume $\qquad V_r = Vm/V_c$

Reduced Temperature $\quad T_r = T/T_c$

critical temperature of a substance is the temperature above which vapor of the substance cannot be liquefied, no matter how much pressure is applied.

critical pressure of a substance is the pressure required to liquefy a gas at its critical temperature.

critical volume is the volume of a unit mass (usually one mole) of a substance measured when it is at its critical temperature and pressure.
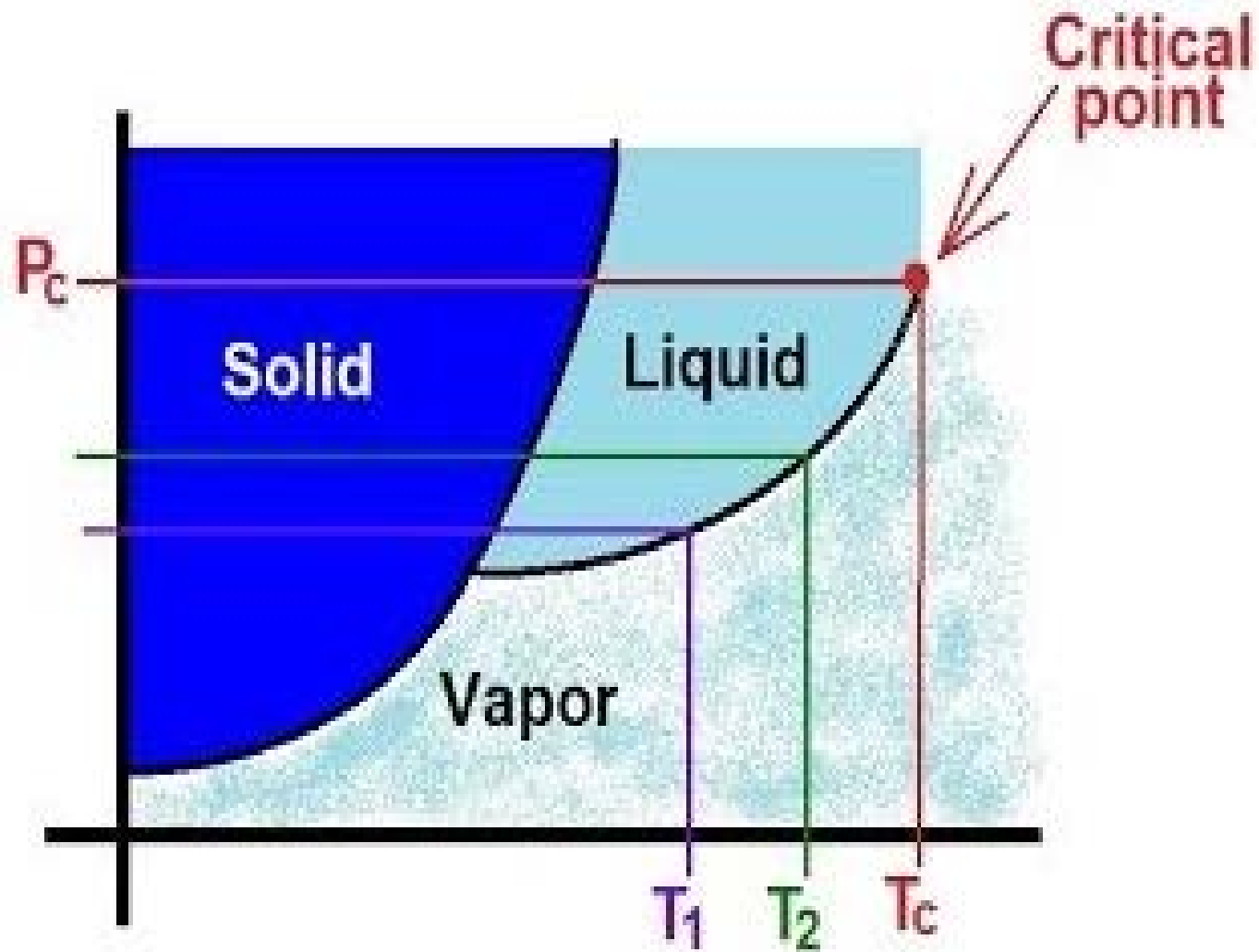
Corrections for Nonideal Behavior

- The ideal-gas equation can be adjusted to take these deviations from ideal behavior into account.

- The Real (non ideal) gas equation is known as the Van der Waals equation.

Corrections for Non-ideal Behavior

- The ideal gas equation contains two factors that could be adapted to be suitable for real gases they are pressure and volume (P, V) .. Van der Waals modified the ideal gas equation by introducing additional terms (are determined by empirical methods) in account for :

☐The volume of the gas molecules.

☐The intermolecular forces between the gas molecules.

Corrections for Nonideal Behavior

1- the effect of attraction forces between molecules:

By adding a term to the pressure in the ideal gas law: $\dfrac{n^2 a}{V^2}$

Where:

        a : constant (different for each gas)

        V : volume of the gas

i.e

the **pressure term** will be $\left(P + \dfrac{n^2 a}{V^2} \right)$

Corrections for Nonideal Behavior

2- The effect of volume occupied by the gas molecules themselves:

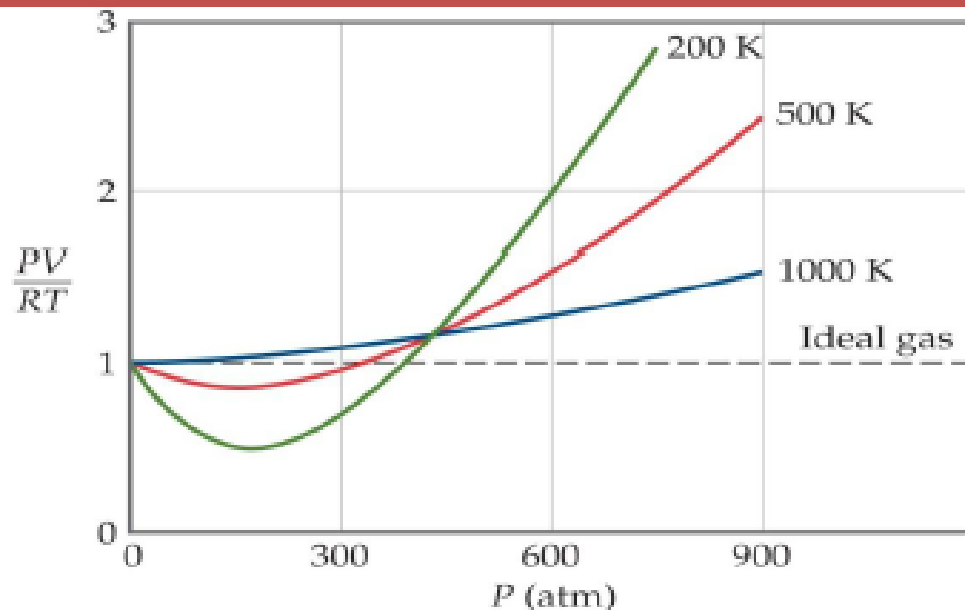By subtracting a term from the **volume** in the ideal gas law: **nb**

Where:

   b : constant (different for each gas)

i.e

the **volume term** will be   **(V – nb)**

Explain the negative deviation from ideal gas behavior of N_2 below 300 atm in this Figure.

Temperature determines how effective attractive forces between gas molecules are in causing deviations from ideal behavior at lower pressures. This Figure shows that, at pressures below about 400 atm, cooling increases the extent to which a gas deviates from ideal behavior. As the gas cools, the average kinetic energy of the molecules decreases. This drop in kinetic energy means the molecules do not have the energy needed to overcome intermolecular attraction, and the molecules will be more likely to stick to each other than bounce off each other.

As the temperature of a gas increases as, say, from 200 to 1000 K in above Figure the negative deviation of PV/RT from the ideal value of 1 disappears. As noted earlier, the deviations seen at high temperatures stem mainly from the effect of the finite volumes of the molecules.

The van der Waals Equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

corrected pressure

corrected volume

Van der Waals equation
Noni-deal gas

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

Where

P : pressure of the gas

V: volume of the gas

T : Absolute temperature K

R: universal gas constant

N : no. of moles

a, b : constant (different for each gas)

The constants of some gases used in van der Waals Equation

Table 10.3   Van der Waals Constants for Gas Molecules

Substance	$a(L^2\text{-atm}/mol^2)$	$b(L/mol)$
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
F_2	1.06	0.0290
Cl_2	6.49	0.0562
H_2O	5.46	0.0305
NH_3	4.17	0.0371
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

Using the van der Waals Equation

If 10.00 mol of an ideal gas were confined to 22.41 L at 0.0 °C, it would exert a pressure of 10.00 atm. Use the van der Waals equation and a previous table to estimate the pressure exerted by 1.000 mol of Cl_2 (g) in 22.41 L at 0.0 °C.

Solution

Analyze We need to determine a pressure. Because we will use the van der Waals equation, we must identify the appropriate values for the constants in the equation.

Plan Rearrange van der Waals equation to isolate P.

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Solve Substituting $n = 10.00$ mol, $R = 0.08206$ L-atm/mol-K, $T = 273.2$ K, $V = 22.41$ L, $a = 6.49$ L^2-atm/mol^2, and $b = 0.0562$ L/mol:

$$P = \frac{(10.00 \text{ mol})(0.08206 \text{ L-atm/mol-K})(273.2 \text{ K})}{22.41 \text{ L} - (10.00 \text{ mol})(0.0562 \text{ L/mol})} - \frac{(10.00 \text{ mol})^2(6.49 \text{ L}^2\text{-atm/mol}^2)}{(22.41 \text{ L})^2}$$

$$= 10.26 \text{ atm} - 1.29 \text{ atm} = 8.97 \text{ atm}$$

Problem

- Calculate the pressure exerted by 84.0 g of ammonia, NH_3, in a 5.00 L container at 200. °C using the van der Waal's equation. The van der Waal's constants for ammonia are: $a = 4.17$ atm L^2 mol^{-2} b $=3.71\times10^{-2}$ L mol^{-1}

Solution

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$n = 84.0g \times 1mol/17$ g $T = 200 + 273$

$P = \dfrac{(4.94mol)(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(473K)}{5 \text{ L} - (4.94 \text{ mol} \times 3.71\text{E-}2 \text{ L mol}^{-1})} - \dfrac{(4.94 \text{ mol})^2 * 4.17 \text{ atm L}^2 \text{ mol}^{-2}}{(5 \text{ L})^2}$

$P = 39.81$ atm $- 4.07$ atm $= 35.74$

$P = 38.3$ atm   7% error

Problem

If sulfur dioxide were an "ideal" gas, the pressure at 0°C exerted by 1.000 mol occupying 22.41 L would be 1.000 atm. Use the van der Waals equation to estimate the "real" pressure.

$$a = 6.865 \ L^2 \cdot atm/mol^2$$
$$b = 0.05679 \ L/mol$$

Solution

First, let's rearrange the van der Waals equation to solve for pressure.

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

R = 0.0821 L·atm/mol·K
T = 273.2 K
V = 22.41 L

$$a = 6.865 \ L^2 \cdot atm/mol^2$$
$$b = 0.05679 \ L/mol$$

$$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

$$P = \frac{(1.000\,\text{mol})(0.08206\,\frac{L\cdot atm}{mol\cdot K})(273.2\,K)}{22.41\,L - (1.000\,\text{mol})(0.05679\,L/mol)} - \frac{(1.000\,\text{mol})^2(6.865\,\frac{L^2\cdot atm}{mol^2})}{(22.41\,L)^2}$$

$$P = 0.989\,\text{atm}$$

The "real" pressure exerted by 1.00 mol of SO_2 at STP is slightly less than the "ideal" pressure.

The critical temperature Tc of nitrous oxide (N_2O) is 36.5 $^\circ$C, and its critical pressure, Pc is 71.7 atm. Suppose that 1 mol of N_2O is compressed to 54.0 atm at 356 K. Calculate the reduced temperature and reduced pressure.using compressability factor to estimate the volume occupied by 1 mole of the gas at 54.0 atm and 356 K.

TC = 36.5 + 273   T= 356 K
Pc= 71.7 atm   P = 54 atm

Pr = 54/71.7 = 0.75   Tr = 1.15

Z = 0.8 = (54* V m) / (0.082 * 356)

Vm = =0.43 L/ 1 mol

Comparison between ideal and real gas

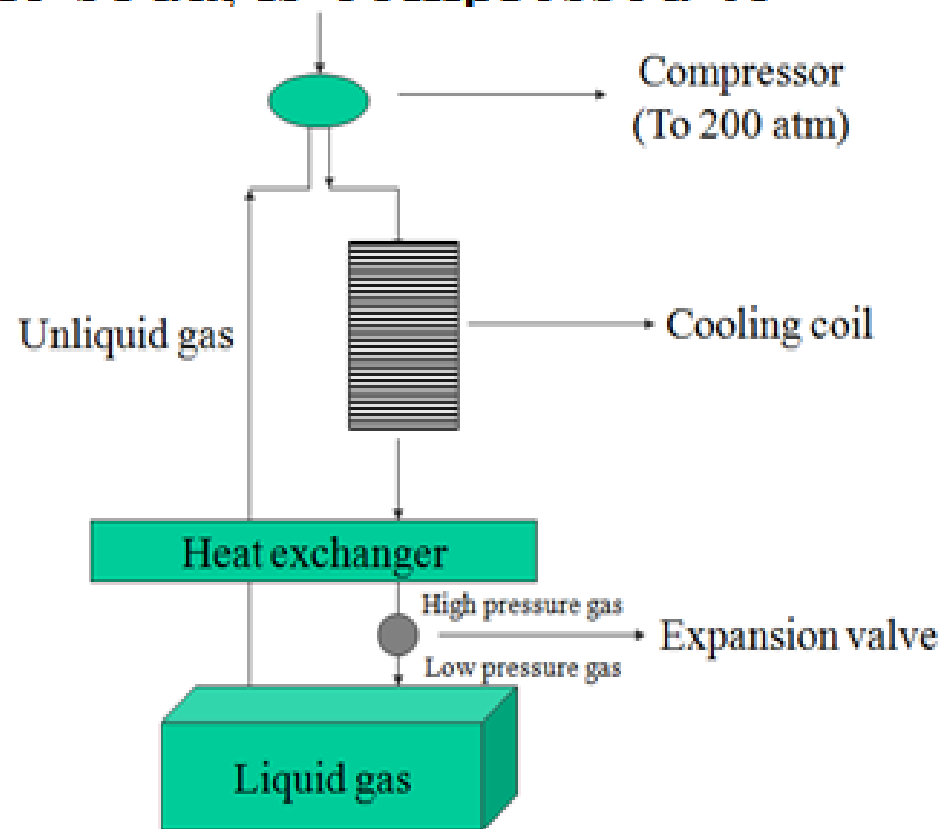| Ideal gas	Real gas
Low pressure	High pressure
High temperature	Low temperature
PV=nRT	PV≠nRT $[P+ (an^2/V^2)]\,[V-nb]= nRT$
There is no Attraction force between molecules	There is Attraction force between molecules
Volume of molecules is neglected compared to the volume of a container	Volume of molecules is not neglected compared to the volume of a container
Compressibility factor (Z)=1	Compressibility factor (Z) ≠1 Z= PV/RT

Liquefaction of gases

A gas can be liquefied by lowering the temperature and increasing the pressure. At lower temperature, the gas, the only available source of energy is that due to the thermal motion of the molecules. Thus the kinetic energy of the molecules will decrease and this must result in a fall in temperature. At ordinary temperatures this cooling effect is, for most gases, extremely small, and as the temperature is raised it becomes even smaller until at one particular temperature characteristic of the gas there is no change in temperature at all.

molecules lose kinetic energy. The slow moving molecules then aggregate due to attractions between them and are converted into liquid. The same effect is produced by the increase of pressure. The gas molecules come closer by compression and coalesce to form the liquid.

At present general principles which employed to liquefy gases is Joule-Thomson effect.
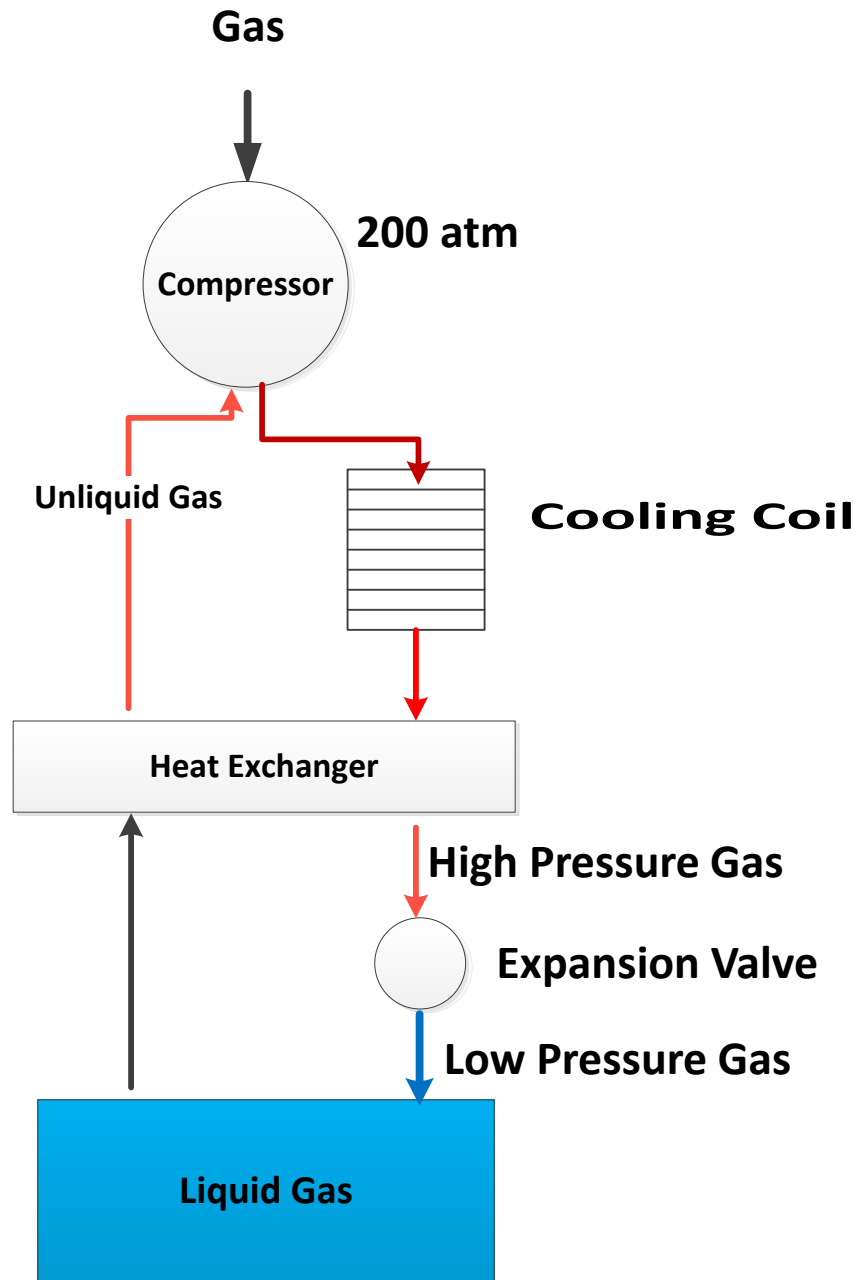
Joule and Thomson in 1854 showed that when a gas under pressure is allowed to pass through a valve or throttle into a region of lower pressure, a cooling effect is observed. This change in temperature, known as the **Joule-Thomson effect,** is a result of the gas not being ideal, and arises from the energy required to overcome the forces of attraction between the molecules in moving them further apart. If the apparatus is effectively insulated from its surroundings

Linde process. Carl von Linde in 1895 successfull[y]

developed a technique for the liquefaction of air. In thi[s]

process (Fig. 1.2) air, previously freed of carbon dioxide b[y]

passage over caustic soda, is compressed to

Compressor
(To 200 atm)

Unliquid gas

Cooling coil

Heat exchanger

High pressure gas

Expansion valve
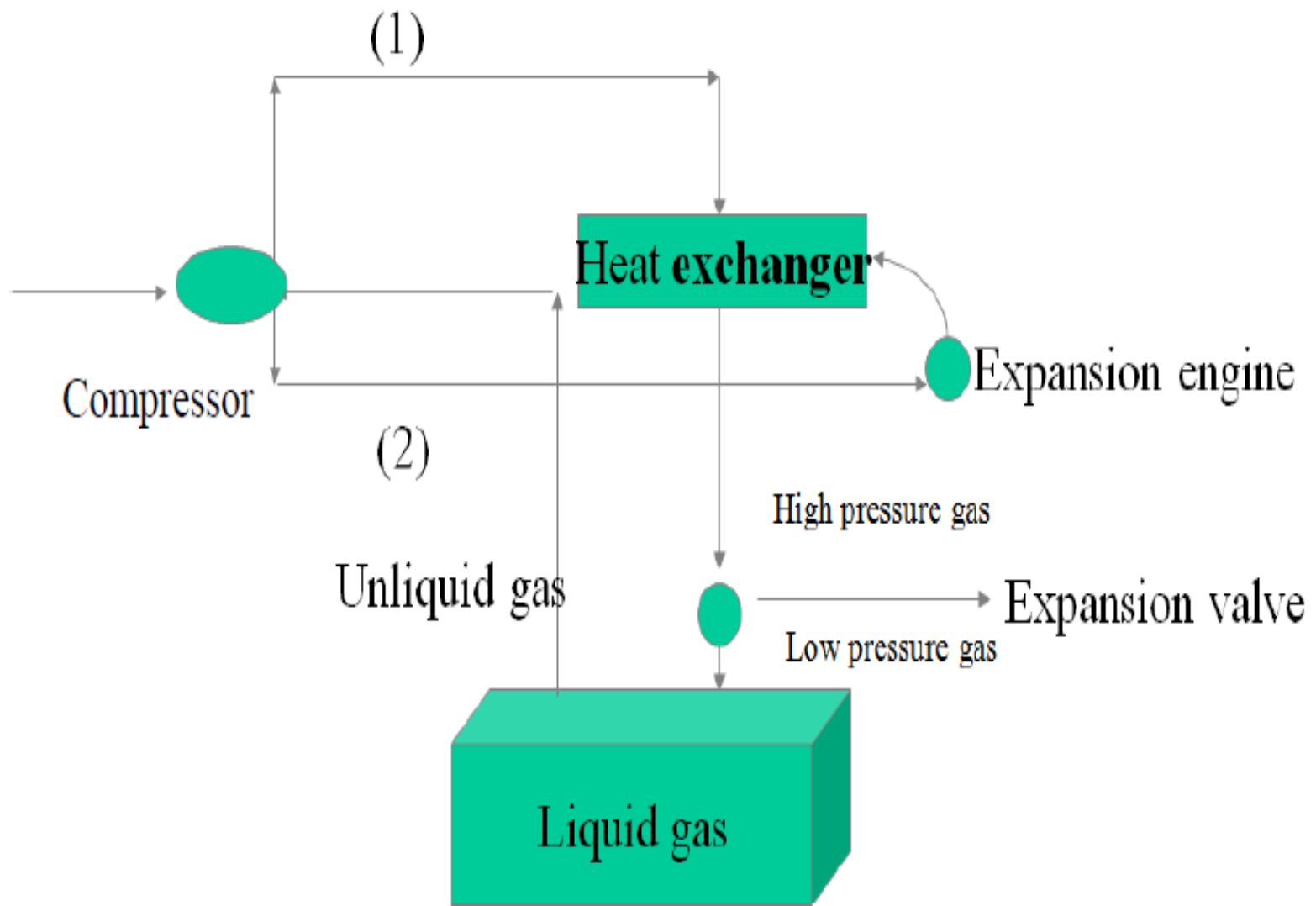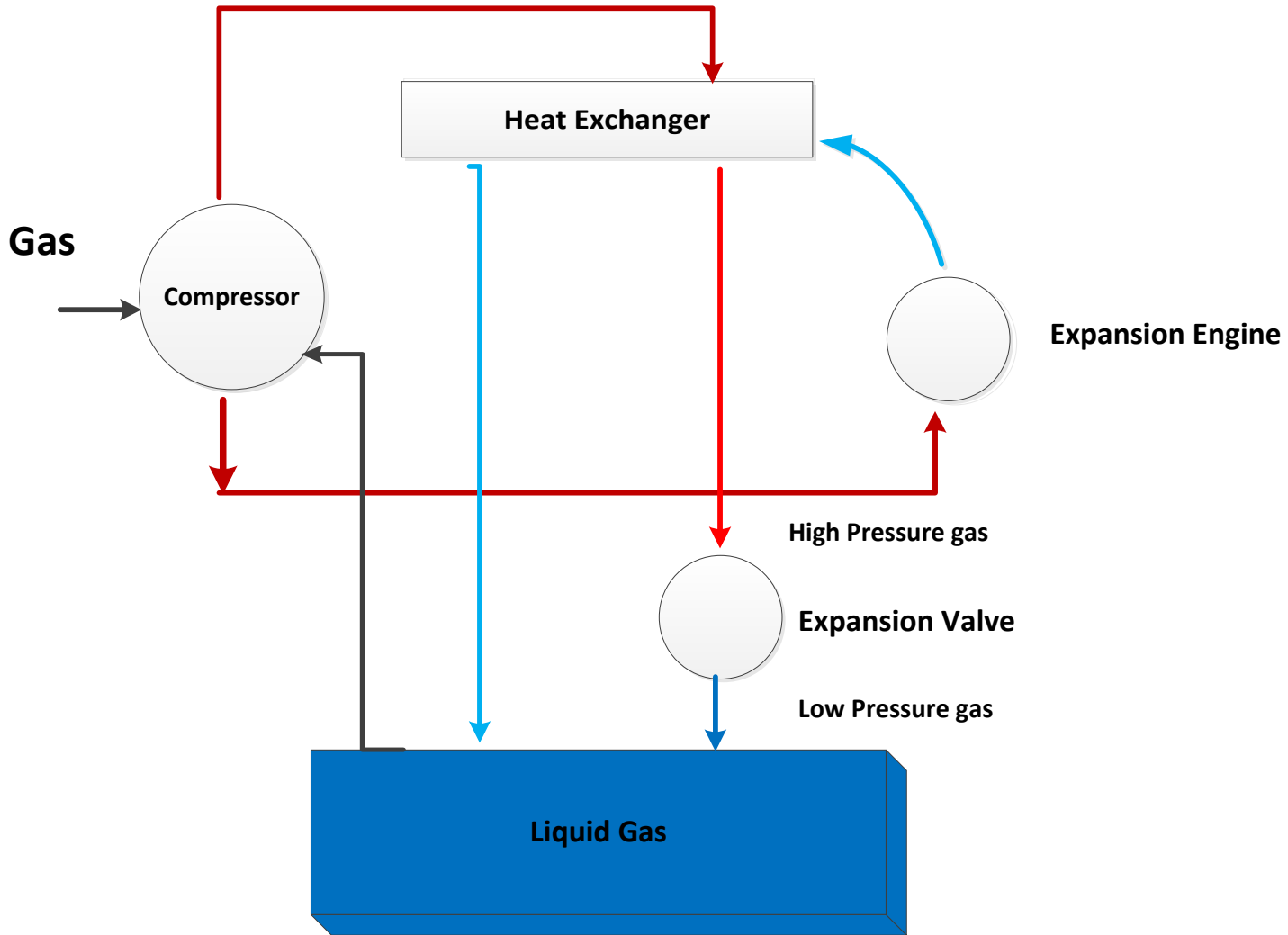
Low pressure gas

Liquid gas

About 200 atm, and passed through cooling coils in order that the heat generated during the compression be removed. The gas stream then passes through the heat exchanger from which it is expanded to about 1 atm through the expansion valve where it is cooled by the Joule-Thomson effect. The gas is then returned to the compressor via the heat exchanger, thus causing the temperature of the incoming compressed gas to be lowered prior to its expansion. The repetition of this cycle results in the temperature of the expanding gas dropping sufficiently to cause partial liquefaction.

The second of the two principles involves cooling by the performance of external work. Consider a gas under pressure enclosed in a cylinder fitted with a piston. When the pressure exerted on the piston is reduced to a value below that of the gas, the latter will expand and cause the piston to move up the cylinder. This performance of work by the gas requires the expenditure of energy. If the expansion is carried out under adiabatic conditions, the performance of mechanical work can only be achieved at the expense of the kinetic energy of the molecules, hence the temperature of the gas drops.

Gas

Compressor

200 atm

Unliquid Gas

Cooling Coil

Heat Exchanger

High Pressure Gas

Expansion Valve

Low Pressure Gas

Liquid Gas

Claude's process; This process is based upon the principle that when a gas expands adiabatically against an external pressure (as a piston in an engine), it does some external work. Since work is done by the molecules at the cost of their kinetic energy, the temperature of the gas falls causing cooling. The air from the compressor is divided into two streams Figure ; one goes to the expansion engine where it is cooled. It is returned to the compressor via the heat exchanger where it pre-cools the second stream of air, the temperature of which is further reduced by its passage through the expansion valve at which point partial liquefaction results.

(1)

Compressor

(2)

Heat exchanger

Expansion engine

Unliquid gas

High pressure gas

Expansion valve

Low pressure gas

Liquid gas

The Clausius- Clapeyron Equation

the vapor pressure of a liquid rise with temperature in a non linear way. A linear relationship is found, however, when the natural logarithm of the vapor pressure (ln P_{vap}), is plotted against the inverse of Kelvin temperature (1/T).

$$\ln(P_{vap}) = [\frac{-\Delta H_{Vap}}{R}][\frac{1}{T}] + C$$

ΔH_{vap} is the heat of vaporization of liquid,

R is the gas constant,

C is a constant characteristic of each specific substance.

When the vapor pressure of a liquid rise to the point where it become equal to external pressure, the liquid boils and changes into vapor.

The temperature at which a liquid boils when external pressure is exactly 1 atm is called the **normal billing point**.

Heat of vaporization the amount of heat required to convert a liquid into a gas at constant temp. and press.

Clausius-Clapeyron equation, which defines the rate vapor pressure change with temperature change:-

$$\frac{dP}{dT} = \frac{H_{vap}}{T\Delta V}$$

Where $dV = V_{vap} - V_{liq}$

$$V = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{H_{vap}}{T[\dfrac{RT}{P}]} = \frac{H_{vap}P}{RT^2}$$

$$\frac{dP}{P} = \frac{H_{vap}}{R}\frac{dT}{T^2}$$

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln \frac{P_2}{P_1} = \frac{H_{vap}}{R}[\frac{T_2 - T_1}{T_1 T_2}]$$

$$\log \frac{P_2}{P_1} = \frac{H_{vap}}{2.303R}[\frac{T_2 - T_1}{T_1 T_2}]$$

Water has ΔH_{vap} = 41 KJ/ mol vapor pressure at 373 K is 101.3 KPa. What is vapor pressure at 298 K?

$$\ln\left(\frac{P1}{P2}\right) = \frac{Hvap}{R}\left(\frac{1}{T2} - \frac{1}{T1}\right)$$

$$\ln\left(\frac{101.3}{P2}\right) = \frac{41000\ J/mol}{8.314\frac{J}{mol.K}}\left(\frac{1}{298} - \frac{1}{373}\right)$$

$$\ln\left(\frac{101.3}{P2}\right) = 3.3272$$

$$\frac{101.3}{P2} = e^{3.3272} \qquad\qquad P_2 = 3.64\ KPa$$

The vapor pressure of ethanol is 115 torr at 34.9° C . if ΔH $_{vap}$ of ethanol is 40.5 KJ/mol . Calculate the temp. when the vapor pressure is 760 torr

P_1 = 115 torr T_1 = 34.9 + 273 = 307.9 K

P_2 = 760 torr T_2 = ?

$$\ln\left(\frac{760}{115}\right) = \frac{-40.5 * 1000}{8.314}\left(\frac{1}{T2} - \frac{1}{307.9}\right)$$

T_2 = 349.6 K