

# GASEOUS STATE

## PART- II

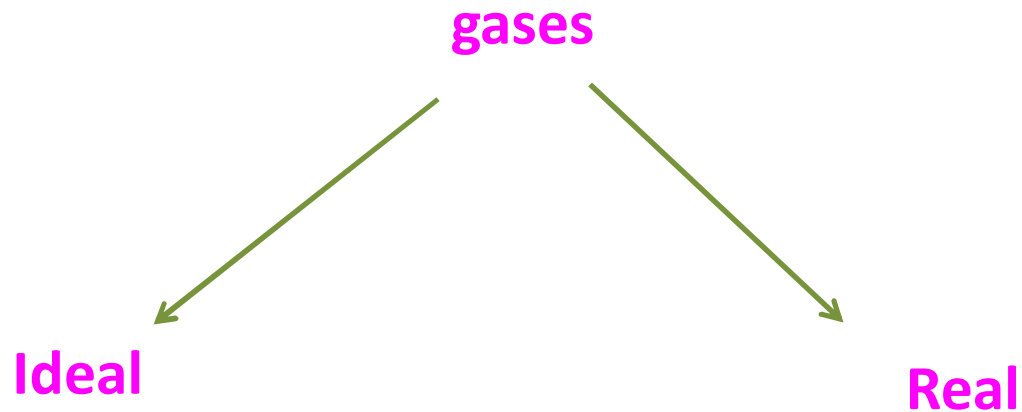
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*Sem I Honours (CC – 2)*

# IDEAL VERSUS REAL GASES



Gases which obey the gas laws under all conditions of temperature and pressure.

Gases which obey the gas laws under limited conditions of temperature and pressure.

At low temperature and high pressure, real gases behave ideally.

# CAUSES OF DEVIATION FROM IDEALITY

- The ideal gas laws are based on kinetic theory of gas which in turn is based on the following two assumptions:

[1] The volume occupied by gas molecules is negligible in comparison to the total volume of the gas.

[2] The gas molecules exert no forces of attraction upon one another.

- As none of the two assumptions are applicable to real gases they show deviation from ideal behaviour.

- Gas can be liquefied and solidified at low temperatures and high pressures. On decreasing temperature, the thermal energy of molecules is decreased and the effect of applying high pressure is to bring the gas molecules close to one another, therefore increasing the forces of attraction among them. Thus, the molecules of a gas occupy a substantial volume which is probably of the same order as that occupied by the same number of molecules in the solid state.
- The molecules of a gas also have weak forces of attraction among them (van der Waal's attraction) which is reflected by the fact that they can be liquefied and solidified. Joule Thomson effect is another proof of existence of attraction force between gas molecules.

# OBSERVATIONS WHICH PROVE DEVIATION FROM IDEALITY

[1] According to Boyle's law, for a given volume of gas at a constant temperature,  $PV = \text{constant}$ .

Thus,  $P$  vs.  $V$  curve should be a rectangular hyperbola. However, at temperature lower than  $T_c$ , the isothermals show two discontinuities. At fairly high temperatures, the isothermals are hyperbolic, although not exactly rectangular.

$$\frac{x^2}{a^2} - \frac{y^2}{b^2} = 1$$

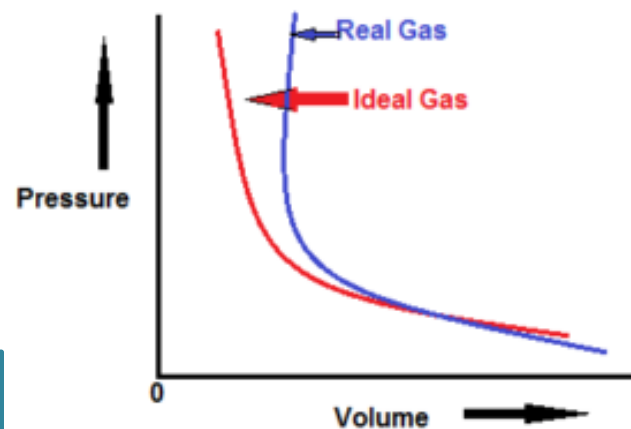
hyperbola

$$\frac{x^2}{a^2} - \frac{y^2}{a^2} = 1$$

rectangular hyperbola

$$xy = c^2$$

rectangular hyperbola if asymptotes are x and y axes



[2] The co-efficient of thermal expansion ( $\alpha$ ) of a gas is given by,  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$

Now,  $PV = nRT \Rightarrow V = \frac{nRT}{P} \therefore \left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}$

$$\therefore \alpha = \frac{1}{V} \cdot \frac{nR}{P} = \frac{1}{V} \cdot \frac{V}{T} = \frac{1}{T}$$

Thus,  $\alpha$  must be a function of  $T$  only and independent of the nature of the gas. However,  $\alpha$  is found to be different for different gases.

At 0°C and 500 atm pressure  $\alpha_{CO_2} = 3.49 \times 10^{-7}$

$$\alpha_{H_2} = 2.78 \times 10^{-7}$$

[3] The co-efficient of compressibility ( $\beta$ ) of a gas is given by,  $\beta = -\left(\frac{\partial V}{\partial P}\right)_T$

Now,  $PV = nRT \Rightarrow V = \frac{nRT}{P} \Rightarrow \left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$

$$\beta = -\frac{1}{V} \left( -\frac{nRT}{P^2} \right) = \frac{1}{P}$$

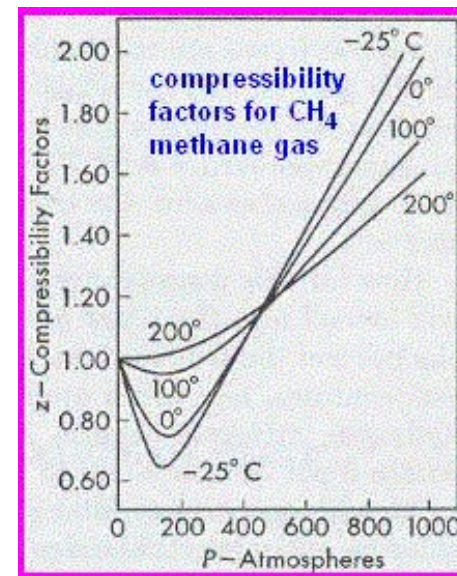
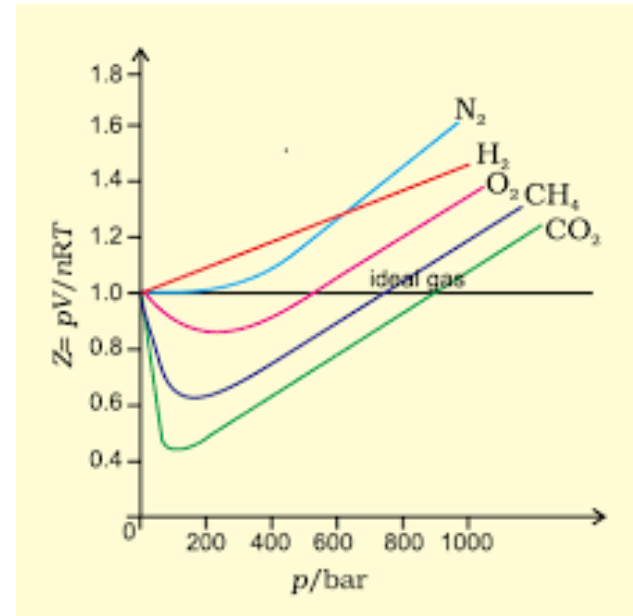
Thus,  $\beta$  should be a function of  $P$  only. Experimentally,  $\beta$  is found to vary with the nature of the gas.

# COMPRESSIBILITY FACTOR

- The deviations can be displayed more clearly, by plotting the ratio of observed molar volume to the ideal molar volume. This ratio is called the **compressibility factor ( $Z$ )**.

$$Z = \frac{V_m}{V_{m,ideal}} = \frac{P}{RT} V_m$$

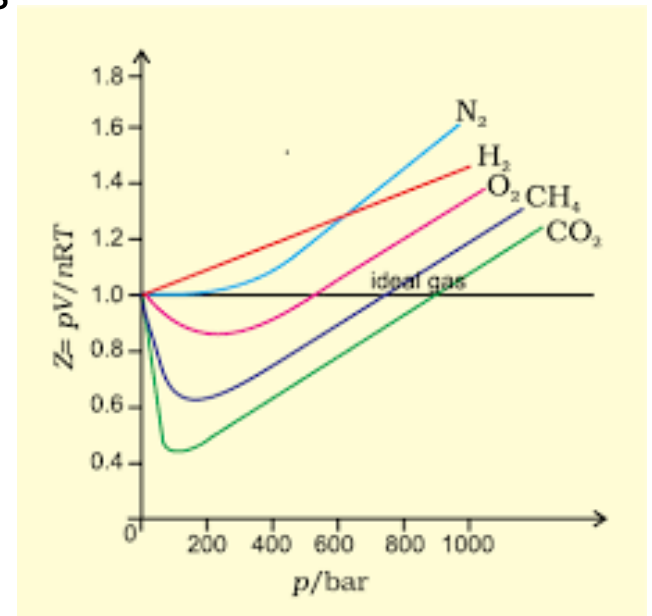
- For an ideal gas,  $Z = 1$  and is independent of  $T$  and  $P$ .
- For a real gas,  $Z = f(T,P)$





From the above plot it is observed that :

- $Z$  is always greater than 1 for  $H_2$
- For  $O_2$ ,  $Z < 1$  in the lower part of the pressure range and  $Z > 1$  in the higher pressure.
- For  $CO_2$ , there is a large dip in the beginning.
- It seems that the nature of  $Z$  vs  $P$  curve depends on the nature of the gas. Actually, it is not so. The determining factor is the temperature relative to the critical temperature ( $T_c$ ) of the particular gas. Near  $T_c$ , the  $P$ - $V$  curves are like that for  $CO_2$ , but when far away, the curves are like that for  $H_2$ .

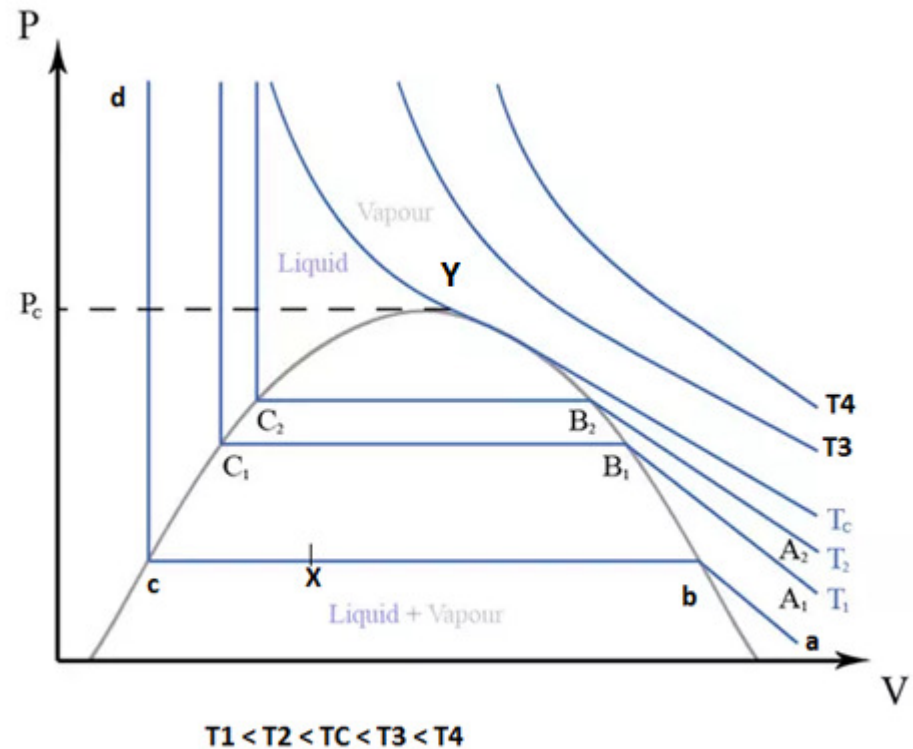


# CRITICAL CONSTANTS

## ANDREW'S ISOTHERM

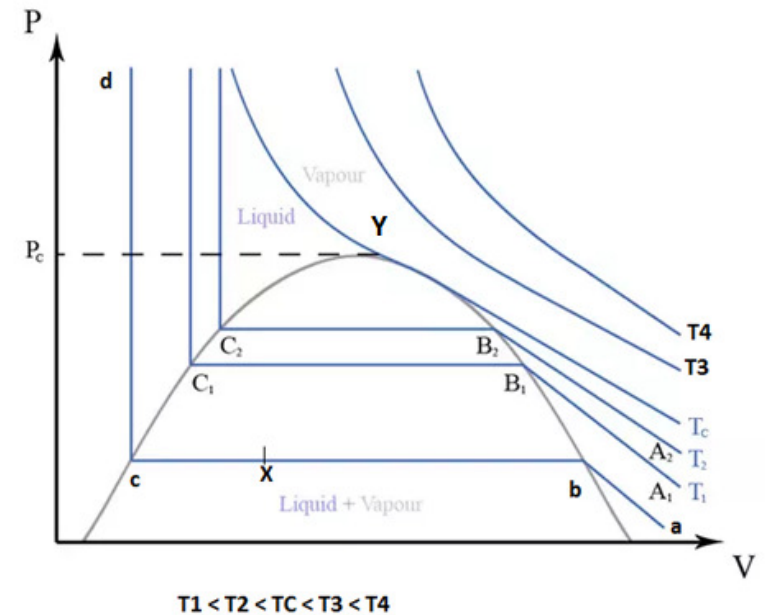
- Thomas Andrews carried out an experiment with  $\text{CO}_2$  to determine  $P$ - $V$  relationship at various temperatures.

- At high temperatures, such as  $T_4$ , the isotherms look like those of an ideal gas.



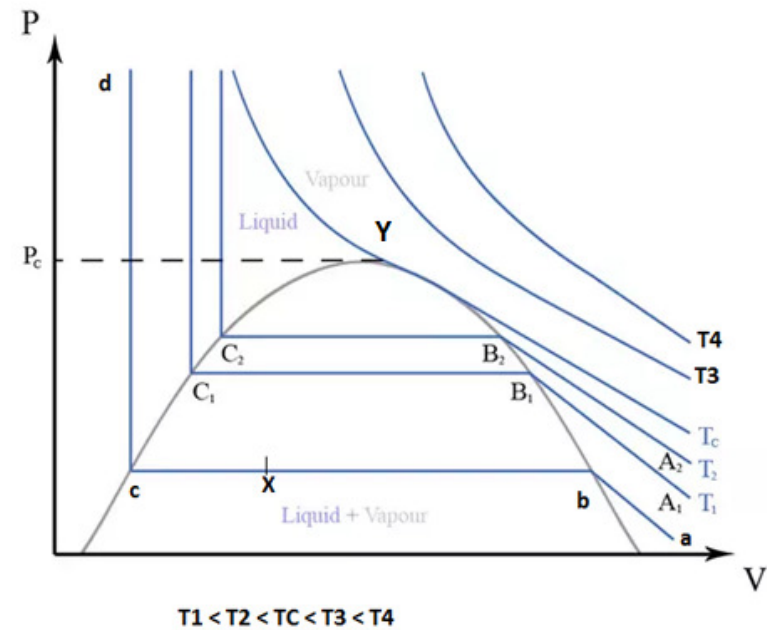
## Curve **abcd**

- **a** → **b**: As pressure increases, volume of the gas decreases.
- at point **b**: **Liquifaction** commences and volume decreases rapidly as the gas is converted to a liquid with a higher density. This takes place at constant pressure.
- At point **c**: **Liquifaction** is complete.
- **c** → **d**: Variation of  $V$  with  $P$  in the liquid state.



- At higher temperature. the nature of the curve is same, except for the fact that the width of the horizontal portion is reduced, the pressure corresponding to this portion being higher than that at lower temperature.
- At  $T_c$ , the horizontal portion is reduced to a point. At temperature greater than  $T_c$ , there is no indication of **liquifaction**.

- At a point between **b** and **c**, say **X**, the ratio of liquid to gas is given by  $bX/cX$ . The pressure corresponding to the line **bc** is known as the vapour pressure of the liquid.

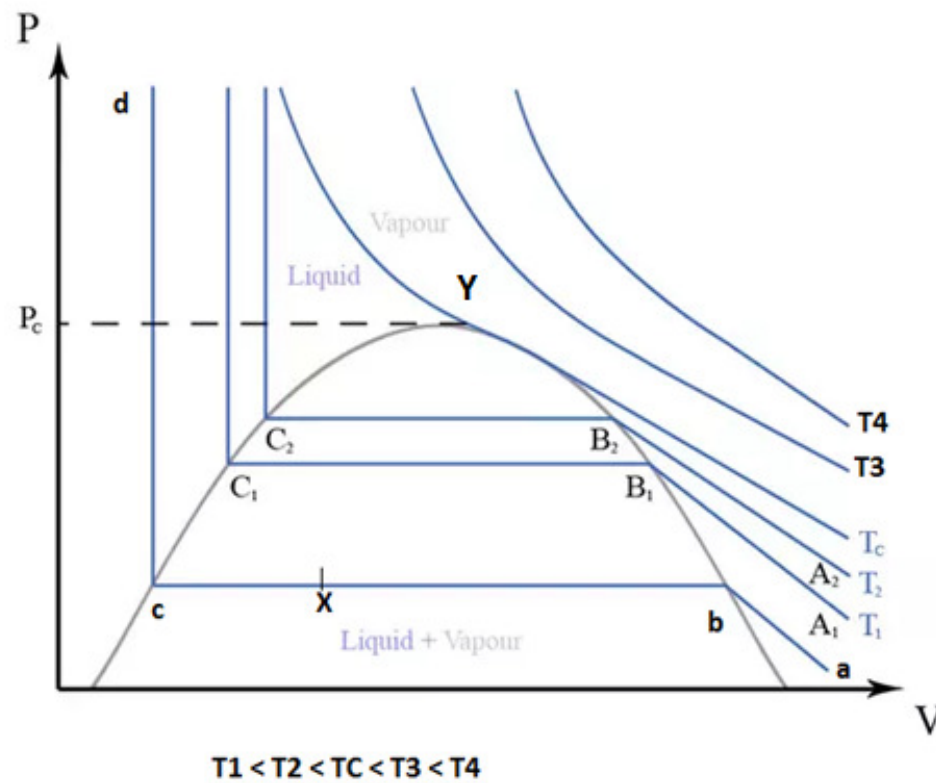


- Point **Y** represents the gas in its critical state. The corresponding isotherm, is known as the critical isotherm. To the left of point **Y** on this isotherm, liquid state exists. At point **Y**, transition from liquid to gas (or vice-versa) takes place and thus it is not possible to state whether the substance is in gaseous or liquid form. Both the states become indistinguishable at critical point and the values of physical properties like density, refractive index etc. have identical values for both the states. The surface of separation between both the states disappears at critical state.

- **CRITICAL TEMPERATURE ( $T_c$ ):** The maximum temperature at which a gas can be liquified, i.e., the temperature above which a liquid cannot exist.
- **CRITICAL PRESSURE ( $P_c$ ):** The minimum pressure required to cause liquifaction of a gas at temperature  $T_c$ .
- **CRITICAL VOLUME ( $V_c$ ):** The volume occupied by 1 mole of a gas at critical temperature and critical pressure.

# DETERMINATION OF CRITICAL CONSTANTS

1. Andrew's method: By plotting  $P$ - $V$  isotherm for a number of temperatures,  $T_c$ ,  $P_c$  and  $V_c$  can be plotted.

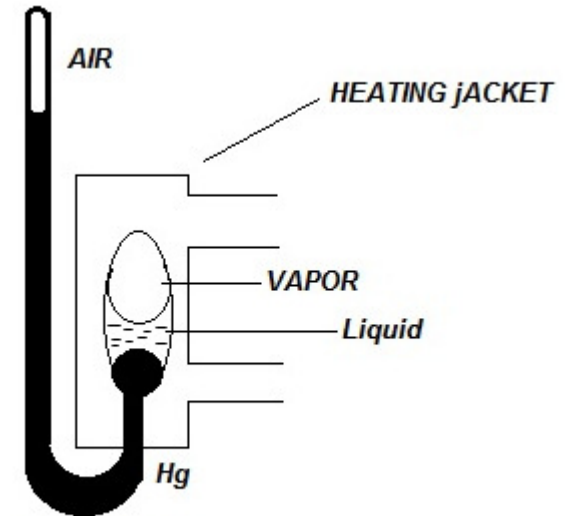


## 2. Determination of $T_c$ and $P_c$

At  $T_c$  and  $P_c$ , the densities of liquid and vapour states become identical and the surface of separation (meniscus) disappears.

Two steps are carried out:

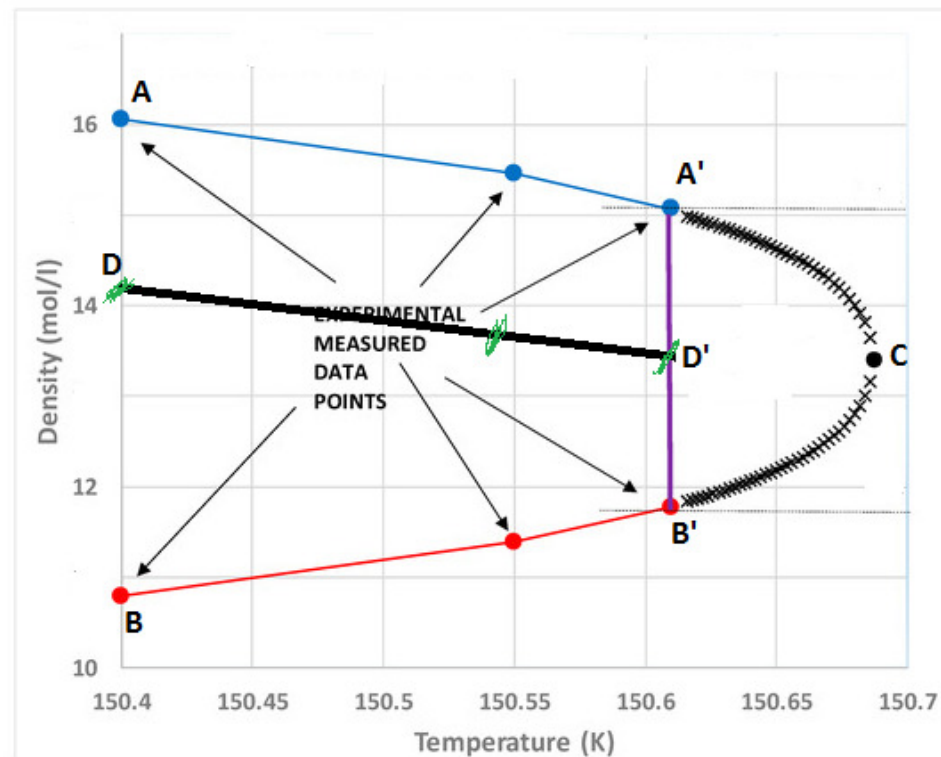
- i) The bulb is cooled so that the surface of separation between liquid and vapour is prominently visible.
- ii) Temperature of the thermostat is gradually increased until the meniscus disappears. The temperature and the corresponding pressure are noted down. The bulb is cooled slowly and again the temperature at which the surface reappears are noted down. The mean of the two temperatures and pressures gives the critical temperature and pressure respectively.



## 2. Determination of $V_c$

With increase in temperature the density of a liquid decreases while the density of its saturated vapour increases. Determination of  $V_c$  is dependent on the law of rectilinear diameter which states that the mean value of the densities of any substance in the state of liquid and of saturated vapour at same temperature is a linear function of temperature.

Mathematically,  $\frac{1}{2}(\rho_l + \rho_v) = a + bt$  where  $a$  and  $b$  are constants.





- On extrapolating AA', BB' and DD', point C is obtained, which gives the value of critical density. From the value of critical density ( $\rho_c$ ), the value of critical volume can be obtained,

$$V_c = \frac{M}{\rho_c}$$

- To determine the densities, a known mass of liquid is enclosed in a graduated tube and heated to a particular temperature volume  $V_l$  and  $V_g$  are obtained from the graduation. If  $\rho_l$  and  $\rho_v$  are the densities of liquid and vapour respectively. Then,

$$m = V_l \rho_l + V_g \rho_g$$

- The experiment is repeated with another mass of the substance at the same temperature.

$$m' = V_l' \rho_l + V_g' \rho_g$$

- Thus,  $\rho_l$  and  $\rho_g$  can be determined.