

## Boyle's Temperature

### Deviation from the Perfect Gas Equation

By the term 'equation of state' is meant the mathematical expression which shows the relation between pressure, volume and temperature of a substance in any state. According to the laws of Boyle and Charles we have for a perfect gas the equation of state

$$pV = RT \quad (1)$$

But even Boyle himself found that the law held only under ideal conditions, viz., at high temperature and low pressure.

### Regnault Experiments

The most earlier studies are carried out by Regnault. He applied pressure up to 30 atmospheres while the temperature was varied from 0° to 100°C. He plotted the product  $pV$  as ordinate against  $p$  as abscissa, as shown in figure 1. From eq. (1) these curve must be straight lines parallel to the pressure axis, since  $pV$  should remain constant. Actually, however, they were found to be inclined to it. Regnault found that for oxygen, nitrogen and carbon dioxide the product  $pV$  decreases with increasing pressure, while for hydrogen it increases. Thus these real gases were shown to be imperfect.

**Figure 1** (a) Variation of  $pV$  versus  $p$  for different gases at low pressure (b) at high pressure.

### Amagat Experiments

Amagat carried out an extensive study of the behaviour of several gases. In his experiments he employed pressure up to 3000 atmosphere. He represented his results by graphs in which  $pV$  denotes the ordinate and  $p$  the abscissa. The curves for  $\text{CO}_2$  are typical of all gases. We shall discuss his result for carbon dioxide as plotted in figure 2.

The finding of his experiments ultimately supports the conclusion drawn by Regnault and Andrews.

1. The isotherm below critical temperature  $T_c$  have a portion of them parallel to the  $pV$  axis. This indicates that the pressure remains constant while the volume varies, and corresponds to the condensation of the gas.

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2. Further it is seen that the curvature of the isotherms decreases as temperature rises.
3. Each of the isotherms has a minimum which first gradually shifts away from the origin towards the right as temperature increases. After a particular temperature it shifts towards the left. The locus of the minima, shown by the dotted curve, is almost parabolic.
4. This parabolic curve would meet the ordinate through  $p = 0$  on an isotherm which will corresponds to the **Boyle temperature**  $T_b$  (for which  $B = 0$ ).
5. Above this temperature, the value of  $pV$  increases steadily so no minima points are found and carbon dioxide behaves like hydrogen. In fact all gases will behave like  $\text{CO}_2$ , only for  $\text{H}_2$  these changes will occur at very low temperatures.

**Figure 2** The  $pV$  isotherms for carbon dioxide obtained by Amagat.

### Onnes Equation of State

K. Onnes, investigated the behaviour of several gases and found that none of the numerous equation of state proposed so far correctly represents the results of above experiments. He found that at any temperature the result is best represented by an empirical equation of the form;

$$pV = A + Bp + Cp^2 + Dp^3 + \dots \quad (2)$$

where  $A, B, C, D, \dots$  are constants for a fixed temperature, but vary with temperature in a complex manner. They are called the *virial coefficients*.  $A$  is called the first virial coefficient,  $B$  the second virial coefficient,  $C$  the third virial coefficient and so on.  $A$  is simply equal to  $RT$  since for  $p \rightarrow 0$ , eq. (2) reduce to that for a perfect gas, i.e., eq. (1).

In his studies, as many as twenty-five constants were used by Onnes. Later, Holborn and Otto studied several gases up to 100 atmosphere in the temperature range  $-183^\circ\text{C}$  to  $+400^\circ\text{C}$ ., and found that only four virial coefficients are sufficient to take.

### Boyle's Temperature

The coefficient  $B$  is of particular importance. For all gases it is found to vary in a similar manner; at low temperature it has a negative value, then as the temperature is raised it gradually increases to zero and becomes positive. The temperature at which  $B = 0$  is called the **Boyle temperature**  $T_B$ , for at this temperature Boyle's law will hold from zero pressure up to quite high pressure because  $C$  and  $D$  are usually negligibly small. Thus, *It is that temperature above which a real gas behaves like an ideal gas and obeys Boyle's law.*

$$\frac{\partial(pV)}{\partial p} = B + 2Cp + 3Dp^2 \approx 0 \quad (3)$$

and  $pV = A = \text{constant} \quad (4)$

At room temperature  $B$  is found to be negative for oxygen, nitrogen and air, and positive for hydrogen and helium, etc.  $C$  is always positive.

For a gas which obeys Vander-Waals equation of state, we have

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

To put Vander-Waals equation in virial form we first rewrite it as

$$\left(p + \frac{a}{V^2}\right) = \frac{RT}{(V - b)} = RT(V - b)^{-1} = \frac{RT}{V} \left(1 - \frac{b}{V}\right)$$

$$p = \frac{RT}{V} \left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V^2}$$

$$pV = RT \left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V}$$

Using binomial theorem, we have

$$\left(1 - \frac{b}{V}\right)^{-1} = 1 + \frac{b}{V} + \frac{b^2}{V^2} + \dots$$

Hence,  $pV = RT + \frac{RTb - a}{V} + \frac{RTb^2}{V^2} + \dots$

At the Boyle's temperature  $T_B$ , the  $pV = RT$ , thus

$$pV = RT + \frac{(RTb - a)}{RT} p + \frac{b^2}{RT} p^2 + \dots \quad (5)$$

On comparing with eq. (2), we get

$$A = RT, \quad B = \frac{RTb - a}{RT} \quad \text{and} \quad C = \frac{b^2}{RT} \quad (6)$$

At Boyle's temperature, the second virial coefficient  $B$  is zero. Hence at  $T = T_B$

$$RT_B b - a = 0 \quad \text{or,} \quad T_B = \frac{a}{Rb} \quad (7)$$

The Boyle temperature of any gas which is obeying the Vander-Waals equation of state can be evaluated by the help of above equation. As it depends on the value of  $a$  and  $b$  of the gases therefore it is different for different gases. For example; the Boyle temperature of nitrogen is  $50^\circ\text{C}$ , for hydrogen it is  $-164^\circ\text{C}$  whereas for helium it is  $-250^\circ\text{C}$ .