The earliest investigation into the relation between pressure, specific volume, and temperature for gases was made by Boyle (1661) who was able to confirm the hypothesis that the volume of a given weight of gas should vary inversely as the absolute pressure if temperature is maintained constant. Thus, within the limits of his experimental error Boyle found that at constant temperature the product pv, pressure times specific volume, has a constant value over a considerable range of pressures. These results are best visualized by plotting values of the product pv as ordinate against values of pressure p itself as abscissa. According to Boyle's experimental findings lines of constant temperature (isotherms) of a gas are *straight* and *horizontal* on this pv, p-plane.

The first rough experiments of Charles (1787) and the subsequent more refined experiments of Gay-Lussac (1802) suggested the possibility

TABLE 1. COMPOSITION OF DRY AIR

GAS	MOL PER MOL DRY AIR		LB PER MOL		LB PER MOL DRY AIR	LB PER LB DRY AIR
Nitrogen	0.7803	×	28.016	=	21.861	0.7547
Oxygen	0.2099	×	32.000	=	6.717	0.2319
Carbon Dioxide	0.0003	×	44.003	=	0.013	0.0004
Hydrogen	0.0001	×	2.016	=	0.000	0.0000
Argon	0.0094	×	39.944	=	0.376	0.0130
	1.0000				28.967	1.0000

COMPOSITION OF ARGON	MOL PER MOL DRY AIR
Argon	0.00933
Neon	0.000018
Helium	0.000005
Krypton	0.000001
Xenon	
	0.00935

of establishing a universal temperature scale such that the product pv *for any gas* is simply proportional to temperature measured on this scale in accordance with Equation 1,

$$pv = BT \tag{1}$$

where B is a constant characteristic of the given gas. Referring to the graphical representation previously described in which the product pv is plotted as ordinate against pressure p as abscissa, the vertical spacing of the isotherms should be such that the ordinates to any two isotherms are in the ratio of corresponding absolute temperatures and therefore in the same ratio for any gas.

Precise measurements by modern methods have shown that the experimental findings of Boyle, Charles and Gay-Lussac are only approximately correct. In the range of sufficiently low pressures the isotherms of gases are indeed *straight* on the pv, p-plane; but they are *not horizontal* in accordance with Boyle's Law, being inclined downward to the right at

relatively low temperatures, upward to the right at higher temperatures. Extrapolation of each isotherm to zero pressure has revealed the remarkable fact that the limiting value of the product pv thus obtained is strictly proportional to absolute temperature as suggested by Equation 1, this strict proportionality providing an accurate basis for the establishment of the absolute temperature scale.

The experimental facts of the preceding paragraph are expressed mathematically by Equation 2,

$$pv = BT - A(T)\,p \tag{2}$$

where

p = absolute pressure, pounds per square foot.

v = specific volume, cubic feet per pound.

B = a constant depending on the molecular weight of the gas.

T = absolute temperature, degrees Fahrenheit.

$A(T)$ = a temperature function called *second virial coefficient*, cubic feet per pound [2].* The name undoubtedly originated from consideration of Clausius' Virial Theorem according to which the mean kinetic energy of a molecular aggregate is equal to the mean value of a quantity, which Clausius called the *virial* of the system, depending solely on the forces acting upon the molecules and not upon the motion of the molecules. This name is used extensively. For some gases, the magnitude of the second virial coefficient can be predicted from theory; but at present, direct experimental measurements are more reliable.

It will appear in what follows that the error committed in computing values of specific volume from Equation 1 instead of Equation 2 is extremely small. Thermodynamically, however, the former would deny the effect of pressure on the thermal properties of a gas which experiment shows to be appreciable. Therefore Equation 1 cannot be made the basis of an accurate analysis.

The numerical value of the constant B in Equation 2 is different for every different gas, but can be calculated if the molecular weight m, pounds per mol, is known; for the product mB is a universal gas constant R, namely,

$$R = 1545.4$$

Example 1. Find the value of B for dry air and water vapor.

Solution. $B_a = 1545.4 \div 28.967 = 53.351$

$B_w = 1545.4 \div 18.0154 = 85.782$

The temperature function $A(T)$, the so-called *second virial coefficient*, expresses the effect of intermolecular forces. It is positive at low temperatures where these forces are predominantly attractive, negative at higher temperatures where they are predominantly repulsive. It is known with satisfactory accuracy for both dry air and water vapor. Values of specific volume are listed in Table 2 for dry air at standard atmospheric pressure (29.921 in. Hg) as computed from Equation 2.

The fact that $A(T)$ is multiplied by pressure in Equation 2 means that intermolecular forces vanish at zero pressure and infinite volume where infinite distances separate the molecules. The finite value of the product pv at zero pressure is due entirely to the translational kinetic

*Bracketed numbers refer to references at end of chapter.