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Boyle's Law, Charles' Law, Rudberg's Law, and the Ideal Gas

The note by A. M. Lesk (*1*) on the relation between $(\partial U/\partial V)_T$ and the equation of state for a gas suggests that the following observations may be of interest.

From the extra-thermodynamic condition $(\partial H/\partial P)_T = 0$, one may obtain using

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \quad (1)$$

Charles' law in the form (*2*)

$$V\mathrm{f}_1(P) = T \quad (2)$$

In eqn. (2) $\mathrm{f}_1(P)$ is an arbitrary function of P. Similarly, from the condition $\partial U/\partial V)_T = 0$, one may obtain using

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (3)$$

the equation

$$P\mathrm{f}_2(V) = T \quad (4)$$

Though no name is usually attached to eqn. (4), it was first experimentally verified by F. Rudberg (*3*). From eqns. (2) and (4) and the idea that an equation of state of the general form

$$\mathrm{f}_3(P,V,T) = 0 \quad (5)$$

exists, $\mathrm{d}T$ is an exact differential and one writes

$$\mathrm{d}T = \left(\frac{\partial T}{\partial P}\right)_V \mathrm{d}P + \left(\frac{\partial T}{\partial V}\right)_P \mathrm{d}V = \mathrm{f}_2(V)\mathrm{d}P + \mathrm{f}_1(P)\mathrm{d}V$$
$$= \frac{T}{P}\mathrm{d}P + \frac{T}{V}\mathrm{d}V \quad (6)$$

Eqn. (6), of course, leads to the gas law for one mole of an ideal gas in the form first proposed by A. Horstmann (*4*)

$$PV = RT \quad (7)$$

The fact that the combination of the restrictions $(\partial H/\partial P)_T = 0$ and $(\partial U/\partial V)_T = 0$ leads to the ideal gas law has been treated in a different way by K. Denbigh (*5*). Eqn. (7) includes Boyle's law

$$PV = \mathrm{f}_4(T) \quad (8)$$

In fact, any two of the three eqns. (2), (4), and (8) together with eqn. (5) allow the third equation to be deduced.

A differential form of Boyle's law is

$$V\left(\frac{\partial P}{\partial V}\right)_T + P = 0 \quad (9)$$

Further, a generating function for eqn. (9) is available from the definition of the enthalpy, since

$$H - U = PV \quad (10)$$

and

$$\left[\frac{\partial(H-U)}{\partial V}\right]_T = V\left(\frac{\partial P}{\partial V}\right)_T + P \quad (11)$$

This gives eqn. (9) if

$$\left[\frac{\partial(H-U)}{\partial V}\right]_T = 0 \quad (12)$$

Literature Cited

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(4) Horstmann, A., *Ann.*, **170**, 192 (1873).
(5) Denbigh, K. G., "The Principles of Chemical Equilibrium," (2nd Ed.), Cambridge University Press, Cambridge, England, **1968**, pp. 107, 462–3.