HANDBUCH DER PHYSIK

HERAUSGEGEBEN VON

S. FLÜGGE

BAND XII

THERMODYNAMIK DER GASE

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Inhaltsverzeichnis.

The Properties of Real Gases.

By

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With 40 Figures.

Notation.

The following symbols are used for the principal thermodynamic functions: E (energy), H (heat content), S (entropy), A (Helmholtz free-energy), G (Gibbs free-energy).

Modifications to these symbols have the following significance:

X An extensive property (except for T).
X Value per mole (except for virial coefficients which are conventionally written in italic).
X^c Value at gas-liquid critical point.
X^g Value in saturated vapour (dew-point).
X^l Value in liquid (bubble-point).
X^* Residual value (Sect. 8).
X_a See Sect. 27.
$X_a^\dagger$ See Sect. 27.
X_a^0 See Sect. 27.

No separate symbol is used for the chemical potential, which is required only in Part VI, as the universally used symbol, μ, is that required for the Joule-Thomson coefficient, which occurs throughout this article.

I. Perfect gases and real gases.

1. Introduction. The atmospheric pressure at the surface of the earth is about 10^6 dyne cm^{-2} and is low in the range of pressures now open to experiment. Early studies of the mechanical and thermal behaviour of gases at and near this pressure soon established that all chemically stable gases behave very much alike. At higher pressures this similarity disappears and the relations between pressure, temperature and volume are still the subject of much careful measurement and subtle theory. The simple laws which all gases were found to obey at atmospheric pressure are those associated with the names of BOYLE and CHARLES[1],

$$p V = k_1 m \qquad \text{(constant temperature, BOYLE)} \tag{1.1}$$

$$V(t_1) - V(t_2) = k_2 m (t_1 - t_2) \qquad \text{(constant pressure, CHARLES)} \tag{1.2}$$

where p and V are the pressure and volume of a mass m of gas, where t is the temperature on some convenient but arbitrary temperature scale, such as a mercury thermometer, and where k_1 and k_2 are constants which vary from gas to gas. When atomic and molecular weights came to be known, it was found that k_1 and k_2 were the same for all gases if m was expressed not in grams but in gram-molecular weights (or moles)—an important law which is still often known as AVOGADRO's hypothesis. If n moles of a substance occupy a volume V, then

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[1] For a brief discussion of these laws and their early history, see J. R. PARTINGTON [10].

the molar volume $\mathrm{V}\,(=V/n)$ may be used in an equation which combines the laws of BOYLE and CHARLES,

$$\frac{p\mathrm{V}}{R'\,T'} = 1\,. \tag{1.3}$$

In this equation T' is the temperature on the gas scale, that is the scale whose zero is at that temperature at which the extrapolated pressure of a gas at constant volume becomes zero. The gas-constant R' depends on the size of the degree in this scale and is almost independent of the nature of the gas. If (1.3) were obeyed exactly, it would be quite independent of the gas. It is found experimentally that it does become independent if the limiting value of $p\mathrm{V}$ at zero pressure is used to define the temperature scale, that is, if the ratio of two temperatures T_1' and T_2' is defined by

$$\frac{T_1'}{T_2'} = \lim_{p\to 0}\left[\frac{(p\mathrm{V})_1}{(p\mathrm{V})_2}\right]. \tag{1.4}$$

The temperature scale defined by this equation is called the perfect-gas scale, and a gas which obeys (1.3) at all temperatures and volumes is a perfect gas. This scale is identical with the absolute scale defined by the second law of thermodynamics[1]. The latter may be determined by measuring the changes in the heat content, H, and the Gibbs free-energy, G, for the same isothermal process. The values of ΔH and ΔG are related by the Gibbs-Helmholtz equation which may be solved as an equation for T, the absolute temperature. In the case of a real gas it is found experimentally that the approach of the product $(p\mathrm{V})$ to the perfect-gas value is linear in p at low pressure, as is illustrated, for example, in Fig. 1. That is,

$$\lim_{p\to 0}\left(\mathrm{V} - \frac{\mathrm{R}T'}{p}\right) = B(T')\,, \tag{1.5}$$

where B is a finite volume which is a function only of the temperature and of the nature of the gas. At low pressures, therefore, the equation of state may be written

$$\mathrm{V} = \frac{\mathrm{R}T'}{p} + B\,. \tag{1.6}$$

Small changes in absolute temperature and pressure in a system of constant mass and composition produce a change in G given by

$$d\mathrm{G} = -\,\mathrm{S}\,dT + \mathrm{V}\,dp \tag{1.7}$$

whence

$$\mathrm{G}(p_1, T) - \mathrm{G}(p_2, T) = \int_{p_2}^{p_1} \mathrm{V}\,dp \tag{1.8}$$

$$= \mathrm{R}\,T'\ln(p_1/p_2) + B\,(p_1 - p_2)\,. \tag{1.9}$$

By differentiation with respect to absolute temperature,

$$\left.\begin{aligned}\mathrm{H}(p_1, T) - \mathrm{H}(p_2, T) = -\,\mathrm{R}\,T^2 \ln\left(\frac{p_1}{p_2}\right)\cdot\left(\frac{d}{dT}\right)\left(\frac{T'}{T}\right)\\ -\,T^2\,(p_1 - p_2)\cdot\left(\frac{d}{dT}\right)\left(\frac{B}{T}\right).\end{aligned}\right\} \tag{1.10}$$

Now it is found for all gases that H, like $p\mathrm{V}$, is a well-behaved function of pressure in the limit of zero pressure. The slope $(\partial\mathrm{H}/\partial p)_T$ has a finite limiting value, as

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[1] The simple method of demonstrating this equality which is given here is that used by E. A. GUGGENHEIM: Thermodynamics, 2nd Ed., p. 88–91. Amsterdam: North Holland Publishing Co. 1950.

may be shown by the isothermal Joule-Thomson experiment described in Sect. 4. No measurement of temperature is made in this experiment. Consequently for this experimental result to be consistent with (1.10),

$$\frac{d}{dT}\left(\frac{T'}{T}\right) = 0, \tag{1.11}$$

or T' is proportional to T. The choice of a common unit for the two scales makes the proportionality an equality.

Thus the concept of a perfect gas fulfils three functions. First, it is a convenient but idealised representation of the behaviour of real gases at normal and moderately high pressures. Secondly, it is a statement of the limiting law of behaviour of all gases at sufficiently low pressures. (This statement must occasionally be modified, but in most senses it is true.) Thirdly, it provides a realisable temperature scale which is identical with KELVIN'S absolute scale. Many of the idealised concepts of physics and chemistry perform functions similar to the first of these, but not to the second. For example, the laws of ideal liquid mixtures are a simple and convenient basis for the discussion of the behaviour of real solutions. There are, however, no conditions of temperature or pressure in which the behaviour of a given real solution becomes ideal. To preserve this distinction it is preferable to call a gas which obeys (1.3) a *perfect* gas, and not an *ideal* gas.

2. The choice of independent variables. The state of a one-component one-phase system is completely specified by two of the three variables, pressure, volume and temperature. In practice, the independent variables are chosen to be either pressure and temperature or volume and temperature. The expressions for the thermodynamic functions in terms of these variables are naturally in their most simple form if the energy, E, the Helmholtz free-energy, A, and the heat capacity at constant volume, C_V, are expressed as functions of V and T, and if the heat content, H, the Gibbs free-energy, G, and the heat capacity at constant pressure, C_p, are expressed as functions of p and T. The entropy, S, can be expressed equally readily in either set of variables.

It is formally possible, in classical statistical mechanics[1], to express the Gibbs free-energy in terms of the partition function of an assembly of constant pressure, temperature and number of molecules by an equation analogous to that expressing the Helmholtz free-energy in terms of the partition function of an assembly of constant volume, temperature and number of molecules, namely,

$$f(V, T, N) = e^{-A/kT}, \tag{2.1}$$

$$f(p, T, N) = e^{-G/kT}. \tag{2.2}$$

Nevertheless only the former function (2.1) has been used in practice for calculating the thermodynamic properties in terms of the intermolecular energies, and the term partition function (or phase integral) is restricted in common usage to $f(V, T, N)$.

Practical convenience often makes one set of variables more suitable than the other. In many cases the design of the apparatus determines whether p or V is to be taken as an independent variable. This can be troublesome near the gas-liquid critical point where $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$ vanish. Here it is preferable to take volume as the variable both when designing an apparatus and when considering the analytical representation of the measurements. The

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[1] E. A. GUGGENHEIM: J. Chem. Phys. 7, 103 (1939). — W. B. BROWN: J. Mol. Phys. 1 (1958) (in the press).

shapes of typical isotherms are shown in Fig. 1 as a function of p and T and in Fig. 2 as a function of $(1/V)$ and T. [The function of (pV/RT), plotted in Fig. 1 and 2, is often called the compressibility factor and denoted Z. The name com-

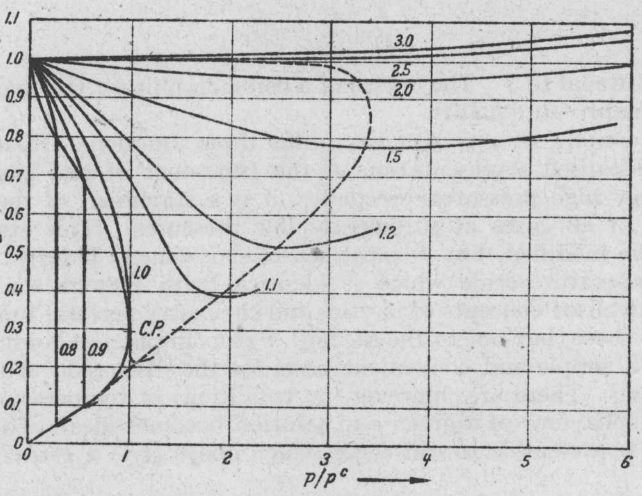

Fig. 1. The compressibility factor, $Z (= pV/RT)$, of the inert gases as a function of pressure for values of T/T^c from 0.3 to 3.0. The tongue-shaped curve on the left of the diagram is the two-phase region. This is crossed by the isotherms below T^c and ends at the critical point (C.P.). The dashed curve is the locus of the Boyle points (see Sect. 10).

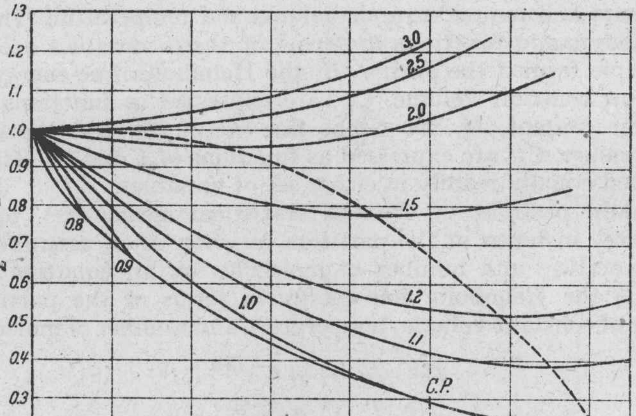

Fig. 2. The compressibility factor, Z, of the inert gases as a function of density for values of T/T^c from 0.8 to 3.0. The two-phase region is that below the lowest curve. The critical isotherm is tangential to this region at the critical point (C.P.). Isotherms at lower temperatures cross this region as rectangular hyperbolae (not shown). The dashed curve is the locus of the Boyle points.

pression factor would be more accurate.] Reduced units have been used in these figures; that is, the ratios p/p^c, T/T^c and V^c/V have been used, where the superscript denotes the value at the critical point. By using these reduced variables the figures can be made to represent qualitatively the behaviour of any fluid.

The curves drawn do, in fact, fit the group of inert gases very closely[1]. It is seen that near the two-phase region the representation of Z as a function of p and T leads to isotherms of very rapidly changing slope and curvature. The representation of Z as a function of $(1/V)$ and T leads to a much smoother family of isotherms whose analytical representation by, say, a polynomial in $(1/V)$ is comparatively easy. The difference between the slopes in the two representations is illustrated by the equations

$$\left(\frac{\partial Z}{\partial(p/p^c)}\right)_T^c = -\infty\,, \tag{2.3}$$

$$\left(\frac{\partial Z}{\partial(V^c/V)}\right)_T^c = -Z^c \approx -0.29\,. \tag{2.4}$$

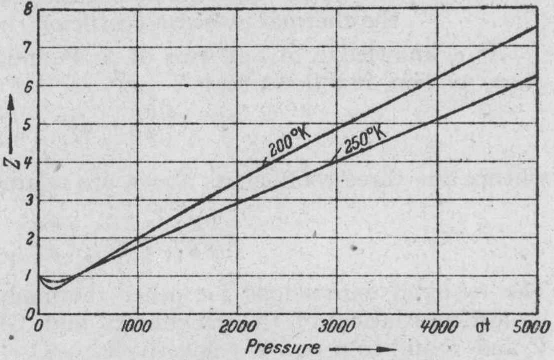

Fig. 3. The compressibility factor, Z, for argon at high pressures (DIN [2]).

The choice of the perfect gas as the standard of normal behaviour is unexceptionable at low and moderate pressures (that is, up to a few hundred atmospheres for most gases), but at very high pressures it is less convenient. Above 1000 atmospheres the molar volume and compressibility of a gas are comparable with those of a liquid near its normal boiling-point, and it is now more convenient to consider V as an explicit function of p and T, rather than to consider departures from (1.3). This is shown in Figs. 3 and 4 where it is seen for argon that (pV/RT) differs widely from unity for pressures above 1000 atmospheres, even at temperatures a long way above the critical temperature of 151° K. However V is here only a slowly varying function of p and T and is comparable with the molar volume of liquid and solid argon at zero pressure.

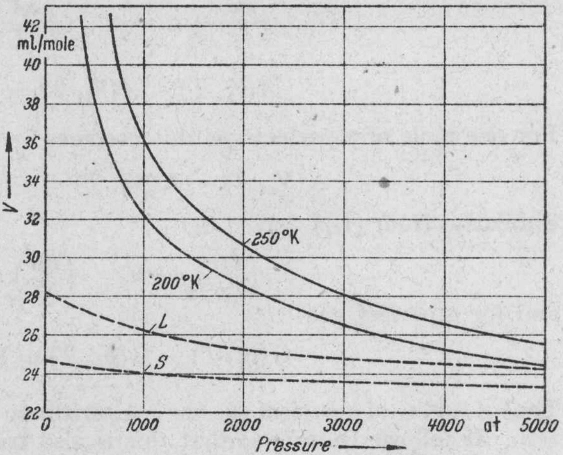

Fig. 4. The molar volume of argon as a function of pressure. The dashed lines are the volumes of the coexisting liquid and solid phases (DIN [2]).

3. The thermodynamic functions of a perfect gas. The pressure, volume and absolute temperature are the three most easily measured properties of a gas. In this section expressions for other thermodynamic properties are derived which contain only these three quantities and their three mutual derivatives. The derivatives are:

$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ the coefficient of cubic thermal expansion, which is often denoted α. In the case of a liquid the derivative is usually evaluated along the coexistence curve. This is scarcely distinguishable from the derivative at constant pressure below the normal boiling-point, but is very different at high pressures.

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[1] J. S. ROWLINSON [11], see Sect. 24.

$\frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ the isothermal coefficient of bulk compressibility, which is often denoted β or $\varkappa_T$. This coefficient is sometimes defined for a liquid as $(-1/V_0)\,(\partial V/\partial p)_T$, where V_0 is the volume extrapolated to zero pressure.

$\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$ which is known in German as the *Spannungskoeffizient*, but which has no recognised name in English, although $(\partial p/\partial T)_V$ is often called the thermal pressure coefficient in the case of a liquid.

As a knowledge of any two of p, V and T determines the third in a one-phase system, it follows that

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT, \tag{3.1}$$

whence the three coefficients above are related by

$$\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial p}{\partial T}\right)_V = -1. \tag{3.2}$$

The required expressions for other thermodynamic functions may be derived by differentiation of the Helmholtz and Gibbs free-energies with respect to V and T and to p and T respectively.

$$dA = -S\,dT - p\,dV. \tag{3.3}$$

Whence

$$\left(\frac{\partial A}{\partial V}\right)_T = -p, \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S \tag{3.4}$$

$$A(V_1, T) - A(V_2, T) = -\int_{V_2}^{V_1} p\,dV. \tag{3.5}$$

For one mole of a perfect gas this becomes

$$\mathrm{A}(\mathrm{V}_1, T) - \mathrm{A}(\mathrm{V}_2, T) = -\mathrm{R}T \ln(\mathrm{V}_1/\mathrm{V}_2). \tag{3.6}$$

Similarly, from (1.7) and (1.8)

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S, \tag{3.7}$$

and for a perfect gas

$$\mathrm{G}(p_1, T) - \mathrm{G}(p_2, T) = \mathrm{R}T \ln\left(\frac{p_1}{p_2}\right). \tag{3.8}$$

Thus A and G of a perfect gas show logarithmic infinities as $(1/V_1)$ and p_1 approach zero. It follows from (1.5) that this is also true for real gases.

From the Gibbs-Helmholtz equation and from (3.4) and (3.7)

$$\left(\frac{\partial E}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V, \tag{3.9}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p. \tag{3.10}$$

These equations, which are sometimes called the *thermodynamic equations of state*, give for isothermal changes in E and H

$$E(V_1, T) - E(V_2, T) = -\int_{V_2}^{V_1} \left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] dV, \tag{3.11}$$

$$H(p_1, T) - H(p_2, T) = \int_{p_2}^{p_1} \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp. \tag{3.12}$$

Both integrands vanish for a perfect gas, for which E and H are therefore independent of volume and pressure, and functions only of the temperature. The independence of E of the volume is JOULE's law and is sometimes made the definition of a perfect gas.

From (3.5) and (3.11) and from (1.8) and (3.12)

$$S(V_1, T) - S(V_2, T) = \int_{V_2}^{V_1} \left(\frac{\partial p}{\partial T}\right)_V dV, \tag{3.13}$$

$$S(p_1, T) - S(p_2, T) = -\int_{p_2}^{p_1} \left(\frac{\partial V}{\partial T}\right)_p dp. \tag{3.14}$$

These are integrated forms of MAXWELL's equations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \tag{3.15}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p. \tag{3.16}$$

For a perfect gas

$$\mathrm{S}(\mathrm{V}_1, T) - \mathrm{S}(\mathrm{V}_2, T) = \mathrm{R} \ln\left(\frac{\mathrm{V}_1}{\mathrm{V}_2}\right). \tag{3.17}$$

The change with temperature of these functions can be expressed in terms of the molar heat capacities at constant volume and at constant pressure,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_V, \tag{3.18}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p. \tag{3.19}$$

For a perfect gas C_V and C_p are independent of volume at constant temperature, as are E and H from which they are derived.

The difference between the heat capcities is given by

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial (E + pV)}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{3.20}$$

whence, from (3.9),

$$C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p. \tag{3.21}$$

This equation may be put into two other forms by using (3.2),

$$C_p = C_V - T\left(\frac{\partial V}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial V}{\partial p}\right)_T, \tag{3.22}$$

$$C_p = C_V - T\left(\frac{\partial p}{\partial T}\right)_V^2 \Big/ \left(\frac{\partial p}{\partial V}\right)_T. \tag{3.23}$$

Eq. (3.21) is the most convenient for calculating $(C_p - C_V)$ for a liquid as the isothermal compressibility is not so readily measured as $(\partial p/\partial T)_V$. Eqs. (3.22) and (3.23) are more convenient for gases; the former being used when the independent variables are pressure and temperature, and the latter when they are volume and temperature. For one mole of a perfect gas these equations give

$$\mathrm{C}_p = \mathrm{C}_V + \mathrm{R}. \tag{3.24}$$

By differentiation of (3.9) and (3.10) with respect to T

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V, \tag{3.25}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p. \tag{3.26}$$

The right-hand sides of these equations are both zero for a perfect gas, but for a real gas only that of (3.25) approaches zero at zero density.

Any fluid may be considered as an assembly of negatively charged electrons and positively charged nuclei interacting solely with Coulomb forces. The application[1] of the virial theorem to such an assembly gives the following relation for the mean kinetic energy of the electrons and nuclei

$$K = 3pV - E = 4pV - H, \tag{3.27}$$

whence

$$K(V_1, T) - K(V_2, T) = \int\limits_{V_2}^{V_1}\left[4p + 3V\left(\frac{\partial p}{\partial V}\right)_T - T\left(\frac{\partial p}{\partial T}\right)_V\right] dV. \tag{3.28}$$

The integrand is zero for a perfect gas but in a real gas the increase in K may be considerable and is generally much larger than the decrease in E.

4. The expansion coefficients of a gas. Much useful information about the thermal properties of a gas can be obtained from a study of the several ways of expanding it. Quotients such as $(\Delta y/\Delta x)$ where x is either pressure or volume, may be determined from expansions. It is usually not difficult to reduce the pressure drop sufficiently to obtain the derivative $(\partial y/\partial x)$ with considerable accuracy. The three most important kinds of expansion are known as the simple (or reversible), the Joule, and the Joule-Thomson expansions. In principle, all may be performed adiabatically or isothermally.

α) Simple expansion. Adiabatic coefficient; $\left(\frac{\partial T}{\partial p}\right)_S$,

Isothermal coefficient; $\left(\frac{\partial S}{\partial p}\right)_T$.

If the pressure of gas in a vessel is suddenly reduced by opening and closing a tap then the gas remaining has undergone an adiabatic expansion in which the maximum work is done in expelling the gas that is lost. The temperature change per unit drop of pressure is therefore $(\partial T/\partial p)_S$. This coefficient was first measured[2] indirectly by DESMORMES and CLÉMENT in 1819 and directly by LUMMER and PRINGSHEIM in 1894. If heat q were to be supplied during the expansion to maintain a constant temperature, then the entropy increase would be (q/T). The isothermal coefficient which, in principle, could be so measured is $(\partial S/\partial p)_T$.

β) Joule expansion. Adiabatic coefficient; $\eta = \left(\frac{\partial T}{\partial V}\right)_E$,

Isothermal coefficient; $\left(\frac{\partial E}{\partial V}\right)_T$.

In 1845 JOULE[2] attempted to detect the change in temperature of a gas on expanding it from one vessel into a second vessel which was initially evacuated. The gas in the first vessel does work, as in the simple expansion above, but

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[1] W. SCHOTTKY: Phys. Z. 21, 232 (1920).

[2] See J. R. PARTINGTON [*10*].

the gas which has flowed into the second vessel has a like amount of work done on it. The net work done in the combined system is zero, so that if the process is performed adiabatically it is an expansion at constant energy, E. The coefficient which is measured is $(\partial T/\partial V)_E$, commonly denoted η. If heat were supplied or withdrawn to maintain the temperature constant, then the coefficient $(\partial E/\partial V)_T$ would be measured.

γ) *Joule-Thomson expansion.* Adiabatic coefficient; $\mu = \left(\frac{\partial T}{\partial p}\right)_H$,

Isothermal coefficient; $\varphi = \left(\frac{\partial H}{\partial p}\right)_T$.

In this expansion[1] the gas is passed continuously through a porous plug or a throttle which maintains a steady pressure drop. In an adiabatic expansion the change in energy, E, must be equal to the work done, that is to the change in $(-pV)$. Thus $H(=E+pV)$ is conserved during the expansion and the coefficient measured is $(\partial T/\partial p)_H$. If, on emerging from the throttle, the gas is heated or cooled at constant pressure to the initial temperature, then the isothermal coefficient is measured, $(\partial H/\partial p)_T$.

The relations between the adiabatic and isothermal coefficients are similar for all three expansions. Equations similar to (3.1) and (3.2) give

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_S = \frac{-C_p}{T}\left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial T}\right)_p, \tag{4.1}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = -\left(\frac{\partial E}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_E = -C_V\left(\frac{\partial T}{\partial V}\right)_E = -p + T\left(\frac{\partial p}{\partial T}\right)_V, \tag{4.2}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H = -C_p\left(\frac{\partial T}{\partial p}\right)_H = V - T\left(\frac{\partial V}{\partial T}\right)_p. \tag{4.3}$$

The last parts of this set of equations follow from (3.16), (3.9) and (3.10). Thus, for a perfect gas, the Joule and Joule-Thomson coefficients vanish, while the simple adiabatic coefficient is given by

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\mathrm{R}T}{p\mathrm{C}_p}. \tag{4.4}$$

5. The velocity of sound. The adiabatic coefficient of bulk compressibility is defined by

$$\varkappa_S = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_S. \tag{5.1}$$

This coefficient can be measured directly for a liquid or a solid[2] but for a gas it is usually determined from the velocity of sound waves of small amplitude. This velocity, W, is given by[3]

$$W^2 = \frac{\mathrm{V}}{M\varkappa_S}, \tag{5.2}$$

where M is the molecular weight of the gas. This equation cannot be expected to hold in the limit of zero frequency where the compressions are more nearly isothermal than adiabatic. Moreover at high frequencies the thermal properties of a gas no longer have the equilibrium values associated with infinitely slow adiabatic changes and so the velocity again departs from that defined by (5.2). This dispersion at high frequencies is due to the length of time needed for translational energy to be converted to rotational and vibrational energy[3]. However,

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[1] See footnote 2, p. 8.

[2] D. Tyrer: J. Chem. Soc. Lond. **103**, 1675 (1913); **104**, 2534 (1914). — L. A. K. Staveley and D. N. Parham: Changements de Phase, p. 366. Paris: Société Chim. Phys. 1952.

[3] H. Kneser: This Encyclopedia, Vol. XI.

there is a wide range of frequencies between these lower and upper limits in which W is independent of frequency and is accurately given by (5.2). This value of W may be regarded as an equilibrium property of the gas.

It follows from equations similar to (3.1) and (3.2) that

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{(\partial S/\partial p)_V}{(\partial S/\partial V)_p} = -\frac{(\partial S/\partial T)_V\,(\partial T/\partial p)_V}{(\partial S/\partial T)_p\,(\partial T/\partial V)_p} \tag{5.3}$$

and so, from (3.2), (3.18) and (3.19)

$$\left(\frac{\partial V}{\partial p}\right)_S = \frac{C_V}{C_p}\left(\frac{\partial V}{\partial p}\right)_T \tag{5.4}$$

or

$$\frac{\varkappa_S}{\varkappa_T} = \frac{C_V}{C_p} \tag{5.5}$$

and

$$W^2 = -\frac{\gamma V^2}{M}\left(\frac{\partial p}{\partial V}\right)_T \tag{5.6}$$

which, for a perfect gas, becomes

$$W^2 = \gamma\frac{RT}{M}. \tag{5.7}$$

where γ is the ratio of C_p to C_V. Thus for a perfect gas W is independent of pressure and approximately proportional to the square root of the absolute temperature.

The difference between $\varkappa_T$ and $\varkappa_S$ may be found from (5.5) and (3.22),

$$\varkappa_T - \varkappa_S = \frac{T}{VC_p}\left(\frac{\partial V}{\partial T}\right)_p^2. \tag{5.8}$$

For a perfect gas this difference is (V/TC_p).

6. Thermodynamic stability. The conditions of mechanical and thermal stability[1] impose certain restrictions on the size and sign of thermodynamic functions. The condition that a phase should be mechanically stable requires that

$$\left(\frac{\partial A}{\partial V}\right)_T < 0, \quad \left(\frac{\partial^2 A}{\partial V^2}\right)_T > 0, \tag{6.1}$$

$$\left(\frac{\partial G}{\partial p}\right)_T > 0, \quad \left(\frac{\partial^2 G}{\partial p^2}\right)_T < 0, \tag{6.2}$$

that is, that p and V must be positive and $(\partial p/\partial V)_T$ negative. At the critical point this derivative is zero. The conditions of stability in this special case are discussed in Sect. 21.

The conditions of thermal stability are

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_V < 0, \quad \left(\frac{\partial^2 G}{\partial T^2}\right)_p < 0, \tag{6.3}$$

that is, that C_p and C_V are both positive. Combining these inequalities with (3.22) gives

$$C_p - C_V \geqq 0. \tag{6.4}$$

The two heat capacities are equal at absolute zero and for a fluid, such as water at 4° C, for which the coefficient of thermal expansion is zero. This coefficient is always positive for a gas and so C_p is always greater than C_V.

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[1] I. Prigogine and R. Defay: Thermodynamique Chimique, Chap. 15 and 16. Liège: Desoer 1950. (English trans. by D. H. Everett. London: Longmans 1954.)

Eq. (6.4) requires that

$$\left(\frac{\partial S}{\partial T}\right)_p \geqq \left(\frac{\partial S}{\partial T}\right)_V > 0, \tag{6.5}$$

and (5.1), (5.4) and (5.8) require that

$$\varkappa_T \geqq \varkappa_S > 0. \tag{6.6}$$

II. The thermodynamic properties of real gases.

7. Reference states and standard states. The properties of a gas which are accessible to direct measurement are derivatives, or functions of derivatives, of the free energies. Thus A and G (and, equally, E, H and S) can only be defined and measured with respect to some arbitrary zero. The term *reference state* is used to denote a real or hypothetical state of a system in which a thermodynamic function is chosen to be zero. The term *standard state* is used to describe a state for which it is convenient to tabulate the increase in any function over its value in the reference state.

Two kinds of reference states and standard states are used. They may either be conditions of the system which are realisable in practice or in principle and each defined by a given temperature and volume (or temperature, pressure, and phase), or they may be hypothetical conditions defined by the perfect-gas laws. Both definitions have their advantages. The former provides the most direct link with experiment and offers fewer chances of confusion in its specification. A simple example of such a reference state is that used by MICHELS and his colleagues [*7*], 0° C and 1 atmosphere pressure, a temperature and pressure which come within their usual experimental range. However tables which cover solid, liquid and gaseous phases are usually based on a reference state of the perfectly ordered crystal at 0° K and zero pressure. Possible contributions to the entropy from nuclear spin factors or isotopic separation are conventionally omitted, except for hydrogen. The extensive tables for eight gases recently published by DIN [*2*] are referred to this state. This is probably the most convenient state for the presentation of a large body of information covering a wide range of pressure and temperature. However tables which cover wide ranges of temperature but do not give the pressure variation usually have standard states based on the perfect-gas laws. If each function is individually corrected to the perfect-gas state at 1 atmosphere then there is no *real* state of the system in which, for example, G, H and S have simultaneously the values tabulated in the standard state, as the correction is not the same for every function. Such a set of standard states is used for gases in the extensive tables of thermodynamic properties published by ROSSINI[1] and his colleagues for the American Petroleum Institute[2] and for the National Bureau of Standards[3], and in the tables of HILSENRATH and his colleagues [*8*]. However the standard states for solids and liquids whose normal boiling points are above 0° C are the real states at 1 atmosphere. The reference state for the heat content in these tables is the hypothetical gaseous state at 0° K. This differs from that of DIN by the latent heat of sublimation.

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[1] For the definition of standard states, see F. D. ROSSINI: Chemical Thermodynamics, Chaps. 19 and 23. New York: Wiley 1950. — L. N. CANJAR and F. D. ROSSINI [*12*]. See also Trans Faraday Soc. **50**, 768 (1954).

[2] Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds. Pittsburgh: Carnegie Press 1950.

[3] Selected Values of Chemical Thermodynamic Properties. Nat. Bur. Stand. Circ. 500, 1952.

8. Residual functions. The presence of the logarithmic infinity in S, A and G at zero pressure makes the direct tabulation of these functions difficult. It is sometimes convenient to choose as reference states the hypothetical perfect gases at the same temperature and either at the same volume or at the same pressure as the real gas. Thus there is a different reference state for every real state of the system. Thermodynamic functions referred to such states are here called residual functions and denoted by a superscript asterisk. The residual functions $X^*(V, T)$ and $X^*(p, T)$ are therefore defined by[1]

$$X^*(V, T) = \int_{\infty}^{V} \left[\left(\frac{\partial X}{\partial V} \right)_T - \left(\frac{\partial X}{\partial V} \right)_T^{\text{perfect}} \right] dV \tag{8.1}$$

$$= \int_{0}^{1/V} \left[\left(\frac{\partial X}{\partial (1/V)} \right)_T - \left(\frac{\partial X}{\partial (1/V)} \right)_T^{\text{perfect}} \right] d\left(\frac{1}{V}\right), \tag{8.2}$$

$$X^*(p, T) = \int_{0}^{p} \left[\left(\frac{\partial X}{\partial p} \right)_T - \left(\frac{\partial X}{\partial p} \right)_T^{\text{perfect}} \right] dp. \tag{8.3}$$

The second expression for $X^*(V, T)$ as an integral over the density is, in practice, more useful than the first. The quantities here called residual functions are sometimes called the internal functions of the gas. The latter name can lead to confusion as the name internal energy is sometimes applied to E, not to E^*, and the name internal pressure to $(\partial E/\partial V)_T$.

The residual pressure defined by (8.1) is

$$p^*(\mathrm{V}, T) = p - \frac{\mathrm{R}T}{\mathrm{V}} = \left(\frac{1}{\mathrm{V}}\right)(p\mathrm{V} - \mathrm{R}T). \tag{8.4}$$

If, however, density is to be used in place of volume, as in (8.2), then it is more useful to introduce a new molar residual, Q^*, defined by an equation analogous to the last part of (8.4),

$$\mathrm{Q}^*(\mathrm{V}, T) = \mathrm{V}(p\mathrm{V} - \mathrm{R}T). \tag{8.5}$$

Q^* is the residual of $(p\mathrm{V}^2)$, less a constant. Thus p^* is the appropriate residual function to use with (8.1) and Q^* the appropriate function with (8.2). By substituting the results of Sect. 3 into (8.1) and (8.2) the following equations for the other molar residual functions are obtained in terms of p^* and Q^*,

$$\mathrm{A}^*(\mathrm{V}, T) = \int_{\infty}^{\mathrm{V}} \left(\frac{\mathrm{R}T}{\mathrm{V}} - p \right) d\mathrm{V} = -\int_{\infty}^{\mathrm{V}} p^* \, d\mathrm{V} = \int_{0}^{1/\mathrm{V}} \mathrm{Q}^* \, d\left(\frac{1}{\mathrm{V}}\right), \tag{8.6}$$

$$\left.\begin{aligned} \mathrm{E}^*(\mathrm{V}, T) &= \int_{\infty}^{\mathrm{V}} \left[T \left(\frac{\partial p}{\partial T} \right)_{\mathrm{V}} - p \right] d\mathrm{V} \\ &= \int_{\infty}^{\mathrm{V}} \left[T \left(\frac{\partial p^*}{\partial T} \right)_{\mathrm{V}} - p^* \right] d\mathrm{V} = -\int_{0}^{1/\mathrm{V}} \left[T \left(\frac{\partial \mathrm{Q}^*}{\partial T} \right) - \mathrm{Q}^* \right] d\left(\frac{1}{\mathrm{V}}\right), \end{aligned}\right\} \tag{8.7}$$

$$\mathrm{S}^*(\mathrm{V}, T) = \int_{\infty}^{\mathrm{V}} \left[\left(\frac{\partial p}{\partial T} \right)_{\mathrm{V}} - \frac{\mathrm{R}}{\mathrm{V}} \right] d\mathrm{V} = \int_{\infty}^{\mathrm{V}} \left(\frac{\partial p^*}{\partial T} \right)_{\mathrm{V}} d\mathrm{V} = -\int_{0}^{1/\mathrm{V}} \left(\frac{\partial \mathrm{Q}^*}{\partial T} \right)_{\mathrm{V}} d\left(\frac{1}{\mathrm{V}}\right), \tag{8.8}$$

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[1] A. Michels, M. Geldermans and S. R. de Groot: Physica, Haag **12**, 105 (1946).

$$C_V^*(V,T) = \int_\infty^V T\left(\frac{\partial^2 p}{\partial T^2}\right)_V dV = \int_\infty^V T\left(\frac{\partial^2 p^*}{\partial T^2}\right)_V dV = -\int_0^{1/V} T\left(\frac{\partial^2 Q^*}{\partial T^2}\right) d\left(\frac{1}{V}\right), \tag{8.9}$$

$$\left.\begin{aligned} G^*(V,T) &= \int_\infty^V \left[V\left(\frac{\partial p}{\partial V}\right)_T + \frac{RT}{V}\right] dV = \int_\infty^V V\left(\frac{\partial p^*}{\partial V}\right)_T dV \\ &= \int_0^{1/V} \left[\frac{1}{V}\left(\frac{\partial Q^*}{\partial (1/V)}\right)_T + 2Q^*\right] d\left(\frac{1}{V}\right), \end{aligned}\right\} \tag{8.10}$$

$$\left.\begin{aligned} H^*(V,T) &= \int_\infty^V \left[T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T\right] dV = \int_\infty^V \left[T\left(\frac{\partial p^*}{\partial T}\right)_V + V\left(\frac{\partial p^*}{\partial V}\right)_T\right] dV \\ &= \int_0^{1/V} \left[\frac{1}{V}\left(\frac{\partial Q^*}{\partial (1/V)}\right)_T + 2Q^* - T\left(\frac{\partial Q^*}{\partial T}\right)_V\right] d\left(\frac{1}{V}\right), \end{aligned}\right\} \tag{8.11}$$

$$C_p^*(V,T) = C_V^*(V,T) - R + T\left(\frac{\partial p}{\partial T}\right)_V^2 \Big/ \left(\frac{\partial p}{\partial V}\right)_T . \tag{8.12}$$

The limiting values of all these residual functions at infinite volume is zero. This may be seen by using the limiting form of the equation of state, (1.6), which shows that the limiting value of Q* is finite and equal to $(RT \cdot B)$. These residual functions are inter-related by equations of the usual kind, viz.,

$$E^*(V,T) - A^*(V,T) = H^*(V,T) - G^*(V,T) = T \cdot S^*(V,T), \tag{8.13}$$

$$\left.\begin{aligned} G^*(V,T) - A^*(V,T) &= H^*(V,T) - E^*(V,T) \\ &= V \cdot p^*(V,T) = (1/V) \cdot Q^*(V,T). \end{aligned}\right\} \tag{8.14}$$

A similar set of expressions may be obtained by substituting the results of Sect. 3 into (8.3). However it is again preferable first to define a residual function with a finite limit at zero pressure by an equation analogous to that defining Q*, or by (8.3)

$$V^*(p,T) = V - \frac{RT}{p} = \left(\frac{1}{p}\right)(pV - RT). \tag{8.15}$$

The other residual functions, defined by (8.3), are expressible in terms of V*

$$G^*(p,T) = \int_0^p \left(V - \frac{RT}{p}\right) dp = \int_0^p V^* dp, \tag{8.16}$$

$$H^*(p,T) = -\int_0^p \left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] dp = -\int_0^p \left[T\left(\frac{\partial V^*}{\partial T}\right)_p - V^*\right] dp, \tag{8.17}$$

$$S^*(p,T) = -\int_0^p \left[\left(\frac{\partial V}{\partial T}\right)_p - \frac{R}{p}\right] dp = -\int_0^p \left(\frac{\partial V^*}{\partial T}\right)_p dp, \tag{8.18}$$

$$C_p^*(p,T) = -\int_0^p T\left(\frac{\partial^2 V}{\partial T^2}\right)_p dp = -\int_0^p T\left(\frac{\partial^2 V^*}{\partial T^2}\right)_p dp, \tag{8.19}$$

$$A^*(p,T) = -\int_0^p \left[p\left(\frac{\partial V}{\partial p}\right)_T + \frac{RT}{p}\right] dp = -\int_0^p p\left(\frac{\partial V^*}{\partial p}\right)_T dp, \tag{8.20}$$