

using an apparatus with less efficient mixing; it was for this reason that the results were considered of insufficient precision for the calculation of B_{12} . However, since in all cases $x_2' < x_2$, a negative value of B_{12} was indicated, in keeping with the predictions of the theory of corresponding states.

To calculate a value of B_{12} from all data⁴ equation (7) was used in conjunction with Coggan's⁵ multi-fit programme using the *Atlas I* computer at the University of Manchester. In terms of the criterion

$$\sum(x_2 \text{ observed} - x_2 \text{ calculated})^2$$

the best value for each set of data, namely -997 for dinonyl phthalate and -540 for squalane, was approximately three times better than the corresponding states value of -158. The value -790 which is five times the theoretical value of B_{12} appears to give a reasonable fit to both systems, particularly when $P-p_2$ approaches 1 atm., and is therefore suggested for calculations in gas-liquid chromatography. There is evidence, however, that structural alterations in the mathematical model would enable a very much more accurate fit of data to be made. The theoretical implications of such a model are at present being examined by Dr. Coggan and myself.

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³ Freeguard, G. F., and Stock, R., *Trans. Faraday Soc.*, **59**, 1655 (1963).

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Joule-Thomson Effect: Non-ideality and Association

It is generally asserted in text-books on thermodynamics and the properties of gases that the Joule-Thomson effect demonstrates conclusively that real gases are non-ideal. This is indeed the case, but not in the sense that usually seems to be understood.

The Joule-Thomson effect is a measure of the extent to which, at constant pressure, the volume of a fixed mass of gas fails to be strictly proportional to the absolute temperature. Such departures from the relation $pV \propto T$ occur in: (i) non-ideal gases in which there is no chemical reaction; (ii) ideal quantum gases at very low temperatures; (iii) associating gases (ideal and non-ideal).

Case (ii) has been considered briefly by Landsberg¹. The purpose of the present communication is to emphasize the relevance of case (iii) (exemplified by the large² Joule-Thomson effect exhibited in experiments³ conducted for another purpose on the associating gas $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$); and to point out that, even when the possibility of association is taken into account, it is still possible to use experimental observations on the Joule-Thomson effect as one of the sources of compelling evidence of non-ideality.

Now whereas for inert non-ideal gases there may be either a decrease or an increase in temperature, in an ideal associating gas the Joule-Thomson expansion always leads to a decrease in temperature. That is, $(\partial T/\partial p)_H = -(\partial H/\partial p)_T/C_p$ is always positive (but, provided that a dimer is one of the associated species present, resembles the value for an inert non-ideal gas in tending to a non-zero limit at low pressures). For increase in pressure at constant temperature leads to increased association, and therefore, since enthalpies of dissociation are positive, to decrease in H . Thus, $(\partial H/\partial p)_T$ for an ideal associating gas is always negative, which implies that $(\partial T/\partial p)_H$ is always positive.

It is found from experiment that in certain cases $(\partial T/\partial p)_H$ is negative, as for hydrogen and helium at room

temperature and atmospheric pressure, which compels the conclusion that these systems are non-ideal, and cannot be ideal associating gases. That is: the Joule-Thomson effect does not of itself demonstrate non-ideality (as distinct from association); but inversion of the Joule-Thomson effect does.

This conclusion is akin to one concerning empirical equations of state. If at low pressures an expression $pV = RT + Bp$ is found to apply, a negative value of B might be attributable to association, to non-ideality, or to both together; but a positive value of B cannot occur for an ideal associating gas, and so is conclusive proof of non-ideality.

The point considered here is one more example of similarities in the effects of non-ideality and of chemical reaction (compare, for example, "deviations from Nernst's distribution law"). It should be emphasized that in particular instances, as indicated here, it is possible to show conclusively that the system considered is non-ideal.

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Effect of Interstitial Atoms on a Lattice-vacancy Diffusional Process

AN investigation has been made of the mechanism of diffusion of chromium into iron-carbon systems over the temperature range 950°-1,265° C. At temperatures above 825° C, the diffusional mechanism of chromium into iron is complicated by a change in crystal structure from a body-centred cubic lattice (α -phase) to a face-centred lattice (γ -phase). At low concentrations of carbon, a lattice-vacancy diffusional mechanism has been postulated, and a moving boundary model set up to represent this condition¹. The results have confirmed that at concentrations of carbon of less than 0.16 per cent only lattice-vacancy diffusion was effective. At concentrations of carbon above this, the interstitial atoms hinder diffusion.

This communication presents results illustrating this effect for concentrations of carbon up to 1 per cent (Table 1).

Fig. 1, a plot of $\frac{\text{diffusivity of chromium in iron } (\gamma\text{-phase})}{\text{diffusivity of chromium in iron } (\alpha\text{-phase})}$

versus concentration of carbon, shows that for concentrations of carbon up to 0.16 per cent this ratio is independent

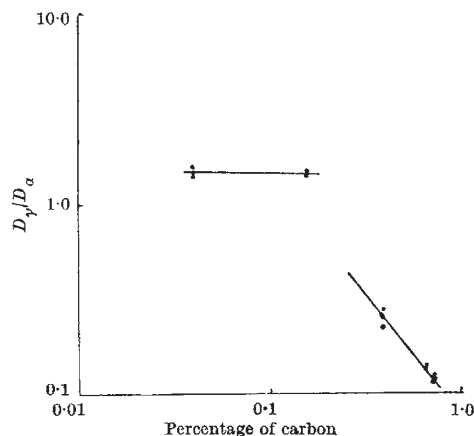


Fig. 1