THERMODYNAMIC CALCULATIONS OF PRESSURE EFFECTS IN GASEOUS REACTIONS BY THE EQUATION OF STATE METHOD. A BRIEF REVIEW[1,2]

L. J. GILLESPIE

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

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The effect of pressure, temperature, and the composition of the equilibrium mixture on the mass-action function K_p is briefly discussed with special reference to published computations for the Haber equilibrium. Improvement in the accuracy of calculations of K_p lies in two directions: improved equations of state for pure gases and improved rules for combining constants (or groups of constants) for the mixture equation. Recent advances in these directions are mentioned.

The basis underlying thermodynamic calculations of the effect of pressure on the yield of a gas reaction may be explained as follows:

It is a general exact principle that an increase of pressure at constant temperature increases the yield of a reaction if the result of the reaction at constant temperature and pressure would be to decrease the total volume of the system.

If the system is one of ideal gases, the equilibrium constant K_p (in terms of the pressure times mole fraction of products) is constant at constant temperature.

If the gases are not ideal, the function K_p is still convenient, though not constant with varying pressure. In this case there is an equation

$$RT\ (\mathrm{d}\ \ln K_p/\mathrm{d}p)_T = (-\delta V/\delta n)_{T,p} - (-\delta V/\delta n)_{T,p,\mathrm{ideal}}$$

the right-hand side of which may be explained as the actual volume decrease minus the decrease as calculated for a mixture of ideal gases, these volume decreases being per mole of some species formed in a supposed infinitesimal shift of equilibrium at constant temperature and pressure.

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[2] Contribution No. 464 from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology.

The species can be any one of the products of the reaction, so long as the chemical equation, to which K_p corresponds, is written for the formation of 1 mole of it.

This equation is rigorously exact, if we note that the derivative on the left is for frozen equilibrium (as is most convenient for calculations) and does not include the small secondary effect of shift of equilibrium on K_p. When integrated, it is equivalent to one already given (2).

The small effect of composition on K_p at constant temperature and pressure cannot be explained in an equally simple manner, since the corresponding equation involves a pressure integration.

The actual volume decreases are not measured. According to the Lewis and Randall fugacity rule, they may be calculated from the actual molal volumes of the various pure species under the assumption that volume changes on mixing the gases at constant temperature and pressure are zero.

Better results are obtained by the use of an equation of state for mixtures, in which the constants for the mixture are calculated from the constants of the pure gases and their mole fractions according to certain combination rules. These rules are somewhat arbitrary but involve no new or arbitrary constants. A summary of these methods has been given in a review (3).

A complete typical application of the method has been made to the Haber equilibrium (4). All available data were smoothed within the experimental error with the use of only two adjustable constants. These may be taken to represent one value of K_p and one value of ΔH. Contrary to an opinion expressed by others, no arbitrary constants were used in the (complete) explanation of the pressure effect (3).

The experiments as well as the calculations are so complete for the Haber equilibrium that some of the results are of general interest in considering the effect of high pressure on gaseous chemical equilibria.

In the first place, the equilibrium yields are already so high at 1000 atmospheres that a beneficial result of increasing the pressure still more would seem to depend principally on an increase of reaction velocity, or on a better balance of engineering factors. At 450°C. and 1000 atmospheres an equilibrium mole per cent of ammonia of 69.4 has been observed (68.6 calculated). This is nearly 82 per cent ammonia by weight.

In considering engineering factors, the effect of pressure on the heat of reaction must not be forgotten. At 500°C. this was calculated to be about 20 per cent for a pressure increase of 1000 atmospheres.

The theoretical effect of a changing hydrogen: nitrogen mole ratio on the value of K_p was found to be small, so long as the ratio is kept at about 3. Thus at 1000 atmospheres no practical benefit on the equilibrium yield can be obtained by using the theoretical optimum ratio instead of the stoichiometrical ratio.

Improvement in the accuracy of calculation of mass-action deviations by the equation of state method lies in two directions: improved equations of state for the pure gases and improved rules for combining constants (or groups of constants) for the mixture equation. Such improvements will doubtless be at the expense of more tedious calculations.

Data on chemical equilibrium are not very helpful in studying possible improvements in the combination rules, as the chemical calculations are not very sensitive to small changes in the rules. What they require most is good $v\ dp$ integrals for the pure gases, and then approximate values for the terms involving volume changes on mixing gases. This is fortunate for the application to chemical problems, but it means that further progress in the problem waits on more p–v–T data, both for pure gases and for mixtures.

A brief discussion of some important work in this field follows.

Benedict, Webb, and Rubin (1) give an equation of state for hydrocarbons (pure) that represents the compressibility to about twice the critical density and also the changes in curvature of the isometrics at about the critical and twice the critical density. Vapor pressures as well as saturation liquid and gas densities may be calculated with extraordinary accuracy.

According to Professor J. A. Beattie, unpublished computations indicate that square-root combination for A_{om} and c_m, together with Lorentz combination for B_{om} and linear combination for a_m and b_m in the Beattie–Bridgman equation for mixtures, gives somewhat the best representation of the compressibility of hydrocarbon mixtures.

An important recent attempt to apply the equation of state method to gases for which individual equations of state are not yet available is that of Keyes (5). He has derived an approximate reduced equation of state which is sufficient for many purposes. He expresses the second virial coefficients in terms of two sets of numerical coefficients—one for polar, and one for non-polar gases—and the critical temperature and pressure of the substance. He also applied the equations to several thermodynamic calculations with surprisingly good results.

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