
A teaching program for gaseous equilibrium

J. D. Lewins

Magdelene College, Cambridge CB3 0AG, UK

E-mail: jdl@eng.cam.ac.uk

Abstract This article demonstrates the use of a teaching program written in MATHCAD[®] which can be converted to other languages in MATLAB[®] by showing samples of the output graphs produced by the program. The program illustrates the minimum of the Gibbs function that governs chemical equilibrium.

Keywords Gibbs function minimum; computer graphs; MATHCAD[®]; MATLAB[®]

Introduction

A teaching program has been written in MATHCAD[®] to be run on a PC, that allows students to explore the nature of the equilibrium reached in gaseous reactions at given pressure and temperature. It is expected that the listing could readily be converted to other languages such as FORTRAN and run on departmental main frames. This has been done in MATLAB[®]. The program allows users readily to choose a reaction of interest and vary the proposed system conditions, seeing the effect on equilibrium proportions.

The theory employed is standard except perhaps for the role of an inert gas diluant in lowering partial pressures and hence in general affecting the equilibrium position. (See the author's article in a companion issue [1], whose illustrations were prepared with this program.) Advantage is taken of computer power not only to evaluate the conventional chemical equilibrium condition point as a function of the extent of reaction but to show directly how this represents a minimum in the system Gibbs function and its relation to the Gibbs function of reaction. An unusual feature is the ability to include an inert diluant gas. In all cases, the chosen conditions are compared with standard conditions of 25 °C, 1 bar and no diluant. The results illustrate the difference between the Gibbs function of standard reaction (where components are all at 1 bar) and the gaseous reaction equilibrium (where the components are at their partial pressures).

Data have been taken from the *Thermodynamic Tables* of Haywood [2] and processed to provide equally spaced temperature intervals from 200 to 6000K for the nine standard reactions he listed.

Input

Reproduced below is the introductory statement made available in the MATHCAD version with guidance on selecting the reaction of interest, or one's own reaction, and selecting system pressure, temperature and degree of dilution with neutral gases. This is accompanied by a warning that if the chosen conditions drive the equilibrium point close to pure reactants or products, then the calculated answers will be

misleading. Strictly, no system can be entirely 'pure' and there will be an equilibrium very close to either 0% or 100% which the program will not evaluate. Results between 1% and 99% are realistic.

GASEOUS EQUILIBRIUM ILLUSTRATED

J. D. Lewins March 2001

This program, written in MATHCAD, illustrates the minimum of the Gibbs function that governs chemical equilibrium. It has data relating to nine well known gaseous reactions, all treated as ideal gases, and can accept data for other such reactions in the form of the stoichiometric coefficients and equilibrium constant ($\ln K_p$) at specified temperatures.

The graphs of (total) Gibbs function against degree of reaction are drawn only to 1% accuracy, to allow a visual assessment of where the equilibrium (or degree of dissociation) lies in any case. Standard pressure is 1 bar in accordance with conventional tables and any different (total) pressure may be entered. The effect of this change of pressure is shown. The system temperature is specified at input of entry in the range 200 to 6000 K. The default temperature is 3000 K and the effect of a change in temperature on equilibrium is shown against 25 °C.

The mixture need not start in stoichiometric proportions. By default, stoichiometric proportions are offered with one hundred kmols times the stoichiometric coefficient of the reactants, zero of the products. Other proportions can be overwritten if desired. The mixture may be diluted with a non-reacting gas (e.g. nitrogen in some reactions but not, for example, the Haber process). If Diluant is chosen, the resulting Gibbs function is compared to that without diluant.

A sub-programme returns the equilibrium position and kmol numbers at a higher accuracy by linear interpolation. In view of the large magnitude of certain of the logarithmic functions close to the end points of the degree of reaction, values within 1% of the end point are not likely to be accurate. This implies avoiding extremes of temperatures. These extremes will differ by reaction number.

Hence the program illustrates the effect of pressure, temperature and diluant on the equilibrium point of mixtures of ideal gases, not necessarily in stoichiometric proportions. Data has been adapted from the Tables (3rd edition) of R A Haywood, Cambridge University Press. The standard reactions are:

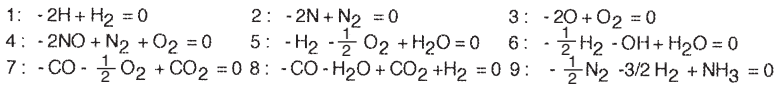
- 1 formation of molecular hydrogen: $-2H + H_2 = 0$
- 2 formation of molecular nitrogen: $-2N + N_2 = 0$
- 3 formation of molecular oxygen: $-2O + O_2 = 0$
- 4 dissociation of nitrous oxide: $-2NO + N_2 + O_2 = 0$
- 5 formation of water (steam): $-H_2 - 1/2O_2 + H_2O = 0$
- 6 reaction of OH radical: $-1/2H_2 - OH + H_2O = 0$
- 7 burning of carbon monoxide: $-CO - 1/2O_2 + CO_2 = 0$
- 8 water gas reaction: $-CO - H_2O + CO_2 + H_2 = 0$
- 9 Haber process: $-1/2N_2 - 3/2H_2 + NH_3 = 0$

n.b. Gibbs functions (although not their differences) have an arbitrary zero. For simplicity, graphs are drawn for the reactant Gibbs function to be zero and then the product Gibbs function would be the Gibbs function of reaction at the chosen pressure – if there is only one component in each of reactant and product.

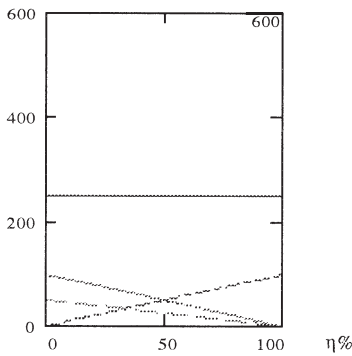
Output graphs

Samples of output graphs for equation 5 (formation of steam from its elements) are reproduced as Figs. 1–6.

Reaction equation q number



Reaction no. $q = 5$ at pressure of $p = 10$ bar and temperature $T = 3 \cdot 10^3$ kelvin
 with diluant of $\text{NL} = 250$ kmols (if $L=1$) $L = 1$
 MOLAR CONCENTRATIONS including Diluant



— diluant
 component 1
 - - - component 2
 - · - component 3
 - · - component 4

Legend valid to $I = 3$
 (if $L=1$, the zeroth value is the unchanging diluant) $L = 1$

equilibrium constant

$$K_{P_0} = 22.021$$

standard Gibbs function of formation

$$\Delta G_0 = -7.712 \cdot 10^4 \text{ kJ per kmol}$$

equilibrium constant at system pressure

$$K_{P_1} = 69.637$$

$S=1$ if stoichiometric proportion (excluding diluant)

$$S = 1$$

Equilibrium percentage composition by kmol

$$n_{eq} = \begin{bmatrix} 0.703 \\ 0.031 \\ 0.015 \\ 0.25 \end{bmatrix} \%$$

Fig. 1 Number of kmol versus extent of reaction %.

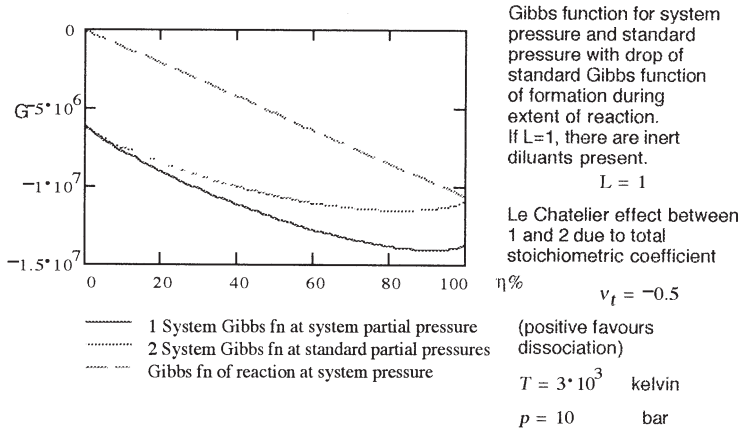
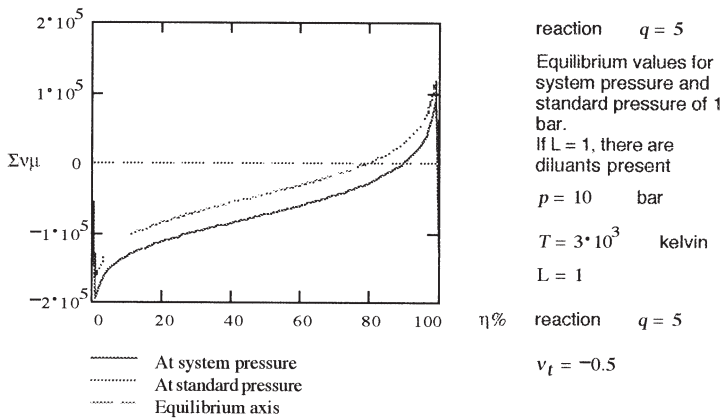


Fig. 2 Gibbs function for reactive mixture showing minimum at equilibrium, versus extent of reaction %.



Equilibrium extent of reaction $\eta_{eq} = 89.46$ % at system pressure

Fig. 3 Stoichiometrically weighted chemical potentials versus extent of reaction showing the vanishing at equilibrium.

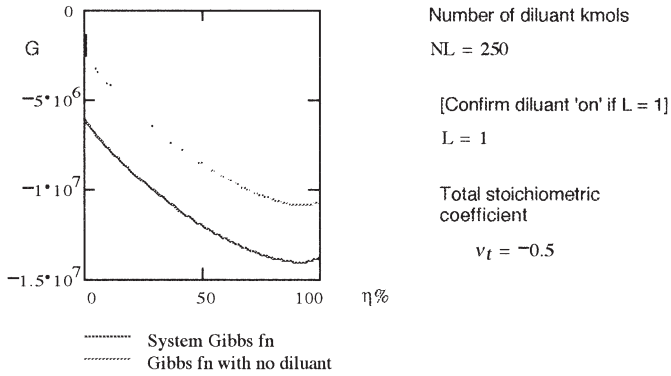


Fig. 4 Gibbs function for system compared to no diluant versus extent of reaction %.

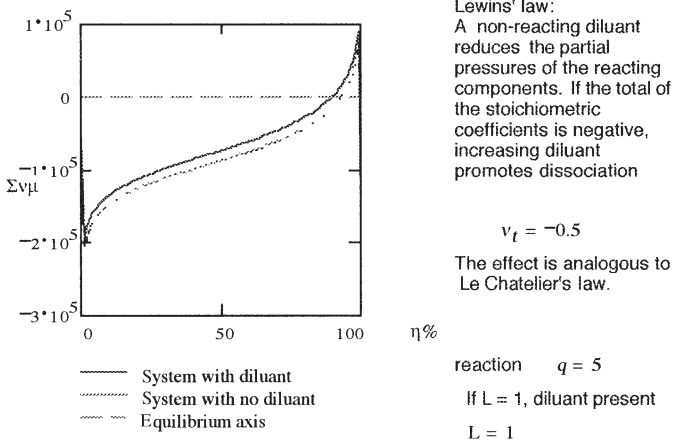


Fig. 5 Effect of diluant on the equilibrium value of the extent of reaction. Stoichiometrically weighted chemical potentials versus extent of reaction.

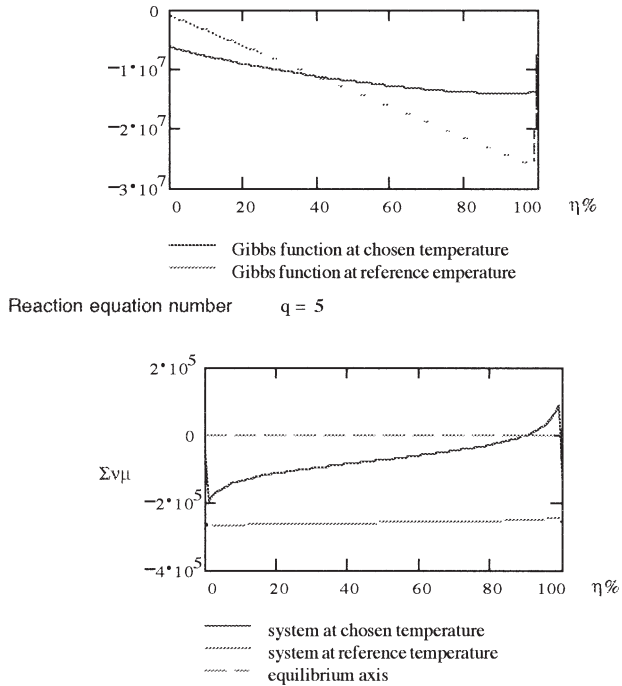


Fig. 6 Comparison of equilibrium at chosen temperature and reference temperature.

System temperature (K) $T = 3 \cdot 10^3$ Reference temperature (K) $T_0 = 298.15$
 Common pressure $p = 10$ bar Diluant present if $L = 1$ $L = 1$

Acknowledgements

Tim Love of the Cambridge University Engineering Department has kindly written the companion program in MATLAB. I am grateful to him and the department for agreeing that both forms, MATHCAD and MATLAB, can be made available at no charge as an attachment to an email reply to such a request, on an undertaking that they will be used for non-commercial, teaching purposes only. Enquires should be made of the author at jdl@eng.cam.ac.uk.

References

[1] J. D. Lewins, 'Gaseous chemical equilibrium', *Int J Mech Eng Education* (in press).
 [2] R. A. Haywood, *Thermodynamic Tables*, 3rd edn (Cambridge University Press, Cambridges, 1990).