[JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA]

Maintenance of Near Equilibrium during Isentropic Expansions through a Nozzle*

BY S. S. PENNER

Introduction

The rates of homogeneous gas reactions in flow systems have been discussed by Benton,[1] Hulburt,[2] and Harris.[3] Brinkley and Weller[4] have recently reported a generalized form of the reaction-rate law in flow systems.

The rates of reactions in flow systems are of considerable importance in the determination of rocket performance.[5,6] During the flow through a rocket nozzle, many chemical reactions occur so slowly, relative to the rate of cooling of the gases, that the chemical composition (mole fraction of each constituent) remains nearly unchanged, thus leading to near-constant-composition flow. On the other hand, some reactions involving atoms or free radicals take place very rapidly, and nearly complete chemical equilibrium may be reached with respect to these rapid reactions at each temperature; *i.e.*, near-equilibrium flow obtains: In general, the rates of all of the chemical reactions which may occur are not sufficient to maintain nearly complete chemical equilibrium during flow, and the flow process as a whole is therefore intermediate between the two extremes mentioned above.

If thermodynamic equilibrium is reached for the chemical reactions in the combustion chamber, then the thrust on the rocket motor will reach a maximum value if complete equilibrium is also maintained during flow through the nozzle. The nature of the flow process can always be determined by a laborious numerical analysis, provided the necessary kinetics data are available.[5,6] Because of the importance of the nature of the flow process through the rocket nozzle on the performance of rockets, it is desirable to derive a simple criterion for determining the existence of near-equilibrium flow and thus obviate the necessity of laborious calculation for many reactions. Accordingly, the present paper is devoted to a discussion of a criterion for near equilibrium during isentropic expansion similar to the criterion developed by Schaefer.[7]

Requirements for Thermodynamic Equilibrium

The present analysis is restricted to a discussion of triple-body collisions[8] which lead to the combination of atoms A and B to form the molecule AB

$$\mathrm{M} + \mathrm{A} + \mathrm{B} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{AB} + \mathrm{M} \qquad (1)$$

where k_f and k_b denote, respectively, the rates of the recombination and dissociation reactions. Assuming the validity of the perfect gas law, the equilibrium constant K_c for reaction 1 is

$$K_c = (\mathrm{AB})/(\mathrm{A})(\mathrm{B}) = K_pRT = k_f/k_b \qquad (2)$$

where (A), (B), and (AB) represent the respective concentrations, K_p is the equilibrium constant defined by the relation

$$K_p = P_{\mathrm{AB}}/P_{\mathrm{A}}P_{\mathrm{B}} \qquad (3)$$

P_{A}, P_{B} and P_{AB} denote the partial pressures of components A, B, and AB, respectively, T is the absolute temperature, and R is the molar gas constant. From equation 2 it can now be seen that flow under conditions of thermodynamic equilibrium is characterized by the relation

$$\mathrm{d}\ln K_c/\mathrm{d}t = \mathrm{d}\ln(\mathrm{AB})/\mathrm{d}t - \mathrm{d}\ln(\mathrm{A})/\mathrm{d}t - \mathrm{d}\ln(\mathrm{B})/\mathrm{d}t \qquad (4)$$

where t represents the time.

Flow through a rocket nozzle is accompanied by changes in pressure and temperature. The concentrations of the reacting components A, B, and AB therefore change for two reasons during flow through the rocket nozzle: (1) a concentration change associated with the change in pressure and temperature (this concentration change occurs without time lag since it depends only on the physical state of the system); (2) a concentration change associated with chemical reaction according to equation 1 [this concentration change depends on the reaction rate constants k_f and k_b and cannot exceed in magnitude the concentration change which has to be added to (1) in order to make the sum of the concentration changes of (1) and (2) equal to the concentration changes required to maintain thermodynamic equilibrium as specified by equation (4)].

It is now necessary to derive analytic relations for the concentration changes defined by (1) and (2).

---

* Presented before the Division of Physical and Inorganic Chemistry at the 114th Meeting of the American Chemical Society in Portland, Oregon, September, 1948.

(1) A. F. Benton, THIS JOURNAL, **53**, 2984 (1931).

(2) H. M. Hulburt, *Ind. Eng. Chem.*, **36**, 1012 (1944); *ibid.*, **37**, 1063 (1945).

(3) G. M. Harris, *J. Phys. and Colloid Chem.*, **51**, 505 (1947).

(4) S. R. Brinkley and S. Weller, THIS JOURNAL, **69**, 1319 (1947).

(5) D. Altman and S. S. Penner, Paper 26 presented before the 112th meeting of the American Chemical Society in New York City, September 1947 (to appear shortly in *J. Chem. Phys.*).

(6) S. S. Penner and D. Altman, *J. Franklin Institute*, **245**, 421 (1948).

(7) K. Schaefer, "On the Thermodynamics of Rocket Propulsion, I," available through Headquarters, Air Materiel Command, Wright Field, Dayton, Ohio, February, 1947.

(8) The recombination of free atoms as the result of collision between two atoms, without the presence of a third body, does not make an appreciable contribution to the number of molecules actually formed, at least not for small atoms such as hydrogen. Chemical reactions other than atomic recombinations generally occur too slowly to allow near-equilibrium flow during expansions through a rocket nozzle. For this reason, only reaction 1 will be considered in this discussion.

Concentration Change Caused by a Change in Temperature and Pressure

The concentration of an idealized gas is a function of pressure and temperature. Only the concentration changes associated with a change of state are considered in this section.

The concentration of the j'th constituent of a system whose physical state is changing is

$$c_j = c_j[p(t), T(t)]$$

where p is the total pressure.

Differentiation with respect to time leads to the result

$$\mathrm{d}c_j/\mathrm{d}t = (\partial c_j/\partial p)(\mathrm{d}p/\mathrm{d}t) + (\partial c_j/\partial T)(\mathrm{d}T/\mathrm{d}t) \quad (5)$$

Adiabatic flow of ideal gases is characterized by the relation[9]

$$\mathrm{d}p/\mathrm{d}T = \gamma p/T(\gamma - 1) \quad (6)$$

where γ is the instantaneous ratio of the specific heat at constant pressure to the specific heat at constant volume. Introducing equation 6 into equation 5 leads to the result

$$\mathrm{d}c_j/dt = \{[p\gamma/T(\gamma - 1)](\partial c_j/\partial p) + (\partial c_j/\partial T)\}(\mathrm{d}T/\mathrm{d}t) \quad (7)$$

Equation 7 will be used only for ideal systems[10] in the present discussion.

The partial pressure p_j of the j'th constituent is

$$p_j = c_jRT = n_jp/n$$

where n_j/n represents the mole fraction of the j'th component. Hence

$$\partial c_j/\partial T = - p_j/RT^2$$

and

$$p(\partial c_j/\partial p) = p[\partial c_j/\partial(np_j/n_j)] = p_j(\partial c_j/\partial p_j) = p_j/RT$$

Replacing $p(\partial c_j/\partial p)$ and $(\partial c_j/\partial T)$ in equation 7, the desired result is obtained

$$\mathrm{d}c_j/\mathrm{d}t = (\gamma - 1)^{-1}(p_j/RT^2)(\mathrm{d}T/\mathrm{d}t) \quad (8)$$

Equation 8 shows the instantaneous concentration change of ideal gases which accompanies a change in pressure and temperature during adiabatic flow.

Concentration Change Caused by Chemical Reaction

For the recombination of atoms according to equation 1, the rate of change of concentration with time for components A, B, and AB is given by the relation

$$\begin{aligned} -\mathrm{d(A)}/\mathrm{d}t &= -\mathrm{d(B)}/\mathrm{d}t = +\mathrm{d(AB)}/\mathrm{d}t \\ &= k_f\mathrm{(A)(B)(M)} - k_b\mathrm{(AB)(M)} \\ &= k_f\mathrm{(A)(B)(M)}[1 - \mathrm{(AB)/(A)(B)}K_c] \quad (9) \end{aligned}$$

From equation 9 it is evident that the rates of concentration change of ideal gases caused by chemical reaction according to equation 1 depend on the rate constants k_f and k_b.

A Criterion for Near-Equilibrium Flow

Flow through a rocket nozzle occurs under conditions where concentration changes are caused by changes in the physical state of the system as well as by chemical reaction. It is therefore necessary to equate the total concentration changes d ln (AB)/dt, −d ln (A)/dt, and −d ln (B)/dt in equation 4 to the sum of the concentration changes given by equations 8 and 9. Thus

$$\begin{aligned} \mathrm{d}\ln\mathrm{(AB)}/\mathrm{d}t &= [(\gamma - 1)T]^{-1}(\mathrm{d}T/\mathrm{d}t) + \\ &\quad k_f[\mathrm{(A)(B)(M)/(AB)}][1 - \mathrm{(AB)/(A)(B)}K_c] \quad (10) \\ -\mathrm{d}\ln\mathrm{(A)}\ \mathrm{d}t &= -[(\gamma - 1)T]^{-1}(\mathrm{d}T/\mathrm{d}t) + \\ &\quad k_f\mathrm{(B)(M)}[1 - \mathrm{(AB)/(A)(B)}K_c] \quad (10a) \\ -\mathrm{d}\ln\mathrm{(B)}/\mathrm{d}t &= -[(\gamma - 1)T]^{-1}(\mathrm{d}T/\mathrm{d}t) + \\ &\quad k_f\mathrm{(A)(M)}[1 - \mathrm{(AB)/(A)(B)}K_c] \quad (10b) \end{aligned}$$

where use has been made of the ideal gas relations

$$P_{\mathrm{AB}}/\mathrm{(AB)}RT^2 = P_{\mathrm{A}}/\mathrm{(A)}RT^2 = P_{\mathrm{B}}/\mathrm{(B)}RT^2 = 1/T$$

Introducing equations 10, 10a and 10b into equation 4 leads to an equation as requirement for thermodynamic equilibrium

$$\begin{aligned} (\mathrm{d}\ln K_c/\mathrm{d}T)(\mathrm{d}T/\mathrm{d}t) &= -[(\gamma - 1)T]^{-1}(\mathrm{d}T/\mathrm{d}t) + \\ &\quad k_f\mathrm{(M)}[\mathrm{(A)} + \mathrm{(B)} + \mathrm{(A)(B)/(AB)}] \times \\ &\quad [1 - \mathrm{(AB)/(A)(B)}K_c] \quad (11) \end{aligned}$$

It is evident from equation 11 that complete thermodynamic equilibrium during expansion, which exists only if

$$\mathrm{(AB)/(A)(B)} = K_c$$

leads to the requirement that k_f is infinite unless

$$-\mathrm{d}\ln K_c/\mathrm{d}T = [(\gamma - 1)T]^{-1}$$

i.e., unless the concentration change associated with a change of state is just sufficient to fulfill the requirements of thermodynamic equilibrium.

The ratio (AB)/(A)(B) at any temperature T may be replaced by the equilibrium constant K'_c at the temperature T'. For equilibrium flow $T' = T$, whereas for near-equilibrium flow $|T' - T|$ is a small number which will be chosen arbitrarily later on. Replacing (AB)/(A)(B) by K'_c in equation 11 leads to the result

$$\begin{aligned} k_f\mathrm{(M)}[\mathrm{(A)} + \mathrm{(B)} + 1/K'_c][1 - K'_c/K_c] &= \\ \{\mathrm{d}\ln K_c/\mathrm{d}T + [(\gamma - 1)T]^{-1}\}(\mathrm{d}T/\mathrm{d}t) \quad (12) \end{aligned}$$

Equation 12 can be simplified by making use of the same artifice employed previously by Schaefer.[7] Thus for sufficiently small values of x, $\ln(1 - x) \simeq - x$. Hence

$$\ln(K'_c/K_c) = \ln[1 - (1 - K'_c/K_c)] \simeq - (1 - K'_c/K_c)$$

or

$$1 - K'_c/K_c \simeq - \ln(K'_c/K_c) \simeq (-\mathrm{d}\ln K_c/\mathrm{d}T)(T' - T) \quad (13)$$

where the approximate equation 13 is the more nearly valid the more closely T' approaches T. From equations 12 and 13 it follows that

$$\begin{aligned} k_f\mathrm{(M)}[\mathrm{(A)} + \mathrm{(B)} + 1/K'_c] &= \{1 + [(\mathrm{d}\ln K_c/\mathrm{d}T) \times \\ &\quad (\gamma - 1)T]^{-1}\}(-\mathrm{d}T/\mathrm{d}t)/(T' - T) \quad (14) \end{aligned}$$

Following Schaefer,[7] near-equilibrium flow

---

(9) Equation 6 is valid even if the composition changes as the result of chemical reaction, provided the heat capacity ratio γ is changed appropriately. The effective heat capacity of the system is redefined to include a term involving the heat release associated with chemical reaction.[6]

(10) An ideal system is defined as a system for which the activity coefficient of each constituent is unity at all times.

through the rocket nozzle is arbitrarily defined by the relation

$$(T' - T) \leqslant 50°\text{K.} \qquad (15)$$

i.e., flow through the rocket nozzle is considered to be near-equilibrium flow if the ratio $(AB)/(A)\cdot(B)$ at the actual temperature T corresponds to the equilibrium ratio at the temperature T' where T' does not differ from T by more than 50°K. Equation 14 thus leads to the following criterion for near-equilibrium flow

$$k_f(M)[(A) + (B) + 1/K_c'] \geqslant 2 \times 10^{-2}\{1 + [(d \ln K_c/dT)(\gamma - 1)T]^{-1}\}(-dT/dt) \qquad (16)$$

Equation 16 differs from the result obtained by Schaefer, who does not consider explicitly the concentration change associated with changes of pressure and temperature. However, criterion 16 can be replaced by Schaefer's criterion in most of the cases which are of interest in connection with adiabatic expansion through a rocket nozzle. Thus the term

$$[(d \ln K_c/dT)(\gamma - 1)T]^{-1}$$

is usually negative and smaller than unity. Therefore if

$$k_f(M)[(A) + (B) + 1/K_c'] \geqslant 2 \times 10^{-2}(-dT/dt) \qquad (17)$$

then inequality 16 is certainly satisfied. Inequality 17 is identical with Schaefer's criterion for near-equilibrium flow. For a more complete discussion of equation 16 it is convenient to note that

$$d \ln K_c/dT = d \ln K_p/dT + 1/T = \Delta H/RT^2 + 1/T$$

where ΔH is negative for the formation of molecules, since heat is evolved during the combination of atoms. Thus equation 16 becomes

$$k_f(M)[(A) + (B) + 1/K_c'] \geqslant 2 \times 10^{-2}\{1 - [(Q/RT - 1)(\gamma - 1)]^{-1}\}(-dT/dt) \qquad (18)$$

where $Q = -\Delta H$.

The following special cases arise:

Case 1. If $Q/RT > 1$ but $[(Q/RT - 1)(\gamma - 1)]^{-1} < 1$, then Schaefer's criterion 17 is applicable. This is the case for most practical applications to adiabatic expansion through a rocket nozzle since $Q \simeq 10^5$ cal./mole, $T \simeq 3000$°K., and $\gamma \simeq 1.2$.

Case 2. If $Q/RT = 1$, then $d \ln K_c/dT = 0$.[11] In this case equation 11 leads to the expression

$$k_f(M)[(A) + (B) + (A)(B)/(AB)] \times [1 - (AB)/(A)(B)K_c] = [(\gamma - 1)T]^{-1}(dT/dt)$$

which requires a definition of near-equilibrium flow different from equation 15. A useful near-equilibrium criterion is obtained by imposing the condition $|(AB)/(A)(B)K_c| \geqslant 0.99$.

Case 3. If $Q/RT < 1$, then equation 18 must be used directly. In particular, if Q/RT is only very slightly less than unity, then the term $[(1 - Q/RT)(\gamma - 1)]^{-1}$ may become very large, and the requirements of inequality 18 are far more stringent than those of inequality 17. This case may be encountered in the future with rocket motors operating at exceedingly high temperatures.

Case 4. If $Q/RT > 1$ and also $[(Q/RT - 1)(\gamma - 1)]^{-1} > 1$, then the right-hand side of equation 18 becomes negative and criterion 18 is no longer applicable. The physical reason for this situation is the fact that the concentration change caused by the change of state is larger than the concentration change required to maintain chemical equilibrium, and therefore reaction according to equation 1 proceeds now from right to left; *i.e.*, molecules must dissociate in order to maintain chemical equilibrium. This case is of no practical importance at present.

As was noted previously, the conditions $Q/RT > 1$ and $[(Q/RT - 1)(\gamma - 1)]^{-1} < 1$ are usually fulfilled during expansion through a rocket nozzle. Therefore Schaefer's criterion 17 is usually applicable and can be used to test for the existence of near-equilibrium flow. Near equilibrium during the entire expansion can be shown to exist if the requirements of equation 17 are fulfilled at each point during flow. In practice, it is sufficient to show that equation 17 holds at a few representative points in the rocket nozzle.

Schaefer's discussion[7] of equation 17 is not applicable for expansions through the nozzles of small rockets[5,6] since $-dT/dt \simeq 3 \times 10^7$ (°K./sec.), rather than $-dT/dt \simeq 5 \times 10^6$ (°K./sec.)., as used by Schaefer.[12] For atomic recombinations as the result of triple collisions, k_f is of the order[7,13] of 10^{11} liter^2 × sec.$^{-1}$ × mole^{-2} at temperatures close to 3000°K.[14] Equation 17 permits determination of the minimum atomic concentrations required for near-equilibrium flow with respect to atomic reactions. Thus if $[(A) + (B)] \geqslant 3 \times 10^7/50 \times 10^{11}(M)$, then near-equilibrium flow will occur. For the adiabatic expansion of gases from a rocket chamber at a pressure of about 20 atm., the total concentration of atoms and molecules $= M \simeq 3 \times 10^{-2}$ (mole/liter) and therefore, $[(A) + (B)] \geqslant 2 \times 10^{-4}$ (mole/liter); *i.e.*, a mole fraction of about 1.5×10^{-2} or greater is required to assure near-equilibrium flow with respect to atomic recombinations. This value for the required mole fraction of atoms is, of course, appreciably greater than the value of 1×10^{-3} arrived at by Schaefer[7] by using too small a value for $(-dT/dt)$. Thus the conclusion is reached that near equilibrium during flow with respect to atomic reactions is strongly dependent on atomic concentrations. Application of the near-equilibrium criterion given in equation 17 to the flow of hydrogen gas through the rocket nozzle for the conditions

---

(11) This condition can be satisfied at only one point if the temperature changes continuously with time.

(12) $-dT/dt$ is decreased as the rocket motor size is increased. Schaefer's value probably refers to the V-2 rocket.

(13) I. Amdur, THIS JOURNAL, **60**, 2347 (1935).

(14) The values of k_f have been measured only at low pressures and for a limited number of reactants A, B, and M. The assumptions that similar rate constants can be used at high pressures for all atomic recombinations in gaseous mixtures, and that the activation energy for the recombination of atoms is zero, are highly questionable and justified only by the lack of better data.

considered previously[6] shows that near equilibrium during flow is maintained in this special case.

Summary

A criterion for near-equilibrium flow during isentropic expansion through a rocket nozzle has been derived. Schaefer's result[7] is shown to be valid for atomic recombinations in a system in which temperature and pressure changes produce concentration changes which are superimposed on the concentration changes associated with chemical reaction provided $-\Delta H/RT > 1$ and $\{[(-\Delta H/RT) - 1](\gamma - 1)\}^{-1} < 1$. These conditions are satisfied in the rocket motors usually encountered. Criteria for near-equilibrium flow under conditions which may be encountered in future work with rockets operating at exceedingly high temperatures are also discussed.

RECEIVED SEPTEMBER 21, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF METALLURGY, UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH]

Extrapolation of Adsorption Isotherms to High Relative Pressures and the Determination of the Surface Pressure of Adsorbed Films on Solids

BY MELVIN A. COOK AND DOUGLAS H. PACK[1]

A recent publication[2] outlined the development of the equation for the unrestricted multimolecular

$$v/v_m = \sum_1^\infty ix^i d_i \Big/ \left(1 + \sum_1^\infty x^i d_i\right) \qquad (1)$$

adsorption of gases on solids. Here the d_i's are a series of interrelated constants different for each adsorbed layer and made up of α_i and β_i components such that $d_i = \alpha_i\beta_i$. The α_i's are factors determined by the energies of interaction of the adsorbate with the surface of the adsorbent, and the β_i's account for the interactions between the adsorbate molecules in the film. Equation (1) differs from the BET[3] equation only in the fact that the d_i's are all the same constant c in the BET theory; the theoretical basis for (1) differs from that of the BET equation only in the description of the adsorption forces.

In reference (2) only the important van der Waals attraction term for the adsorbate–adsorbent interactions, varying as r_i^{-3} (r_i = distance of the i^{th} layer from the surface of the solid), was taken into account, the repulsive and second and higher order attractive terms being neglected. In this approximation the α_i's were defined by the equation

$$\alpha_i = \exp.\ E_1(1 + 1/8 + 1/27 + \ldots + 1/i^3)/RT \qquad (2)$$

where E_1 is the (final) adsorbate–adsorbent interaction energy in the (nearly filled) first layer evaluated as an empirical constant. The β_i's were defined as

$$\beta_i = \exp.\ E_L(c_1 + c_2 + c_3 + \ldots c_i - i)/RT \equiv$$
$$\exp.\ E_L(c_1 - 1)(1 + {}^1/_2 + {}^1/_3 + \ldots + 1/i)/RT \qquad (3)$$

where E_L is the heat of condensation in the corresponding bulk liquid state of the adsorbate and the c_i's are constants related to the empirical constant c_1 as shown. Equation (3) was developed semi-empirically from the consideration that entropy variations in the various layers of the adsorbed film may be related to the average coördination number ratios between an *i-layer* film and the bulk liquid.

On the above basis equation (1) was found to reproduce quite accurately four experimental isotherms over the range from 0.05 to about 0.7–0.8 in relative pressure $x = p/p_0$, the experimental data in these cases being taken only in this range. More recently equation (1) has been examined by comparing it with some experimental isotherms in which the experimental data covered the entire range of relative pressures ($0 < x < 1.0$). Employing the definitions of d_i (equations (2) and (3)), equation (1) was found to reproduce the isotherm over the range from $x = 0.05$ to $x \cong 0.8$, but it predicted too much adsorption for $x > 0.9$ and too little adsorption for $x < 0.05$. It is considered that the discrepancies in the very low pressure region involve a fundamental weakness of the theory incurred by its failure to take account of (1) surface heterogeneities, and (2) the non-constancy of β_1 for various stages of filling of the first adsorbed layer. The discrepancies in the very high relative pressure region on the other hand apparently involve only the deliberate approximations in α_i and evidently may be largely eliminated by simply taking into account the repulsive term.

The present article introduces a simple modification of equation (2) including a theoretical repulsive term, and illustrates the utility of equation (1) in extrapolating isotherms to the relative pressure $x = 1.0$. Also, it seemed worth while to discuss in this article some of the convergence–divergence characteristics of equation (1) and to outline some methods designed to render the equation tractable in practical applications.

Repulsive Term in α_i.—According to approximate quantum mechanical treatments, the repulsive term in the van der Waals interaction should have the form $B_r e^{-r/\rho}$(B_r and ρ being

---

[1] This work was supported by a grant from the University of Utah Research Fund.

[2] M. A. Cook, THIS JOURNAL, **70**, 2925 (1948).

[3] S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).