k_2', k_5, K' = reaction velocity constants for photochemical reactions, consistent units

$m, m_1, m_2, \bar{m}$ = average chain length, that is number of molecules per initiating free radical

(RH) = concentration of hydrocarbon, moles/liter

t = irradiation time, min.

LITERATURE CITED

1. Allen, A. O., "The Radiation Chemistry of Water and Aqueous Solutions," Van Nostrand, New York (1961).
2. Ballantine, D. S., *BNL-294* (*T-50*), (March, 1954); *BNL-317* (*T-53*) (October, 1954); Brookhaven National Laboratory, Upton, New York.
3. Bernstein, I. A., E. C. Farmer, W. G. Rothschild, and F. F. Spalding, *J. Chem. Phys.*, **21**, 1303 (1953).
4. Bouby, L., A. Chapiro, M. Magat, E. Migirdicyan, A. Prevot-Bernas, L. Reinisch, and J. Sebban, in "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva (1955)," Vol. 7, p. 526, United Nations, New York (1956).
5. Charlesby, A., "Atomic Radiation and Polymers," Pergamon, Oxford, England (1960).
6. Chapiro, A., "Radiation Chemistry of Polymeric Systems," Interscience, London, England (1961).
7. Chu, J. C., S. L. Wang, S. L. Levy, and R. Paul, "Vapor-Liquid Equilibrium Data," J. W. Edwards, Ann Arbor, Michigan (1956).
8. *F.I.A.T. Final Report No. 1300.*
9. Harmer, D., Ph.D. thesis, Univ. of Mich., Ann Arbor, Michigan (1955).
10. Kharasch, M. S., T. H. Chao, and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 2394 (1940).
11. Little, Inc., "Radiation—A Tool for Industry," USAEC, Washington, D. C. (1959).
12. "Radiation Processing of Chemicals," *Chem. & Eng. News*, 80-91 (April 22, 1963).
13. Schneider, A., and J. C. Chu, *Ind. Eng. Chem. Process Design Develop.*, **3**, 164 (1964).
14. Stauff, J., *Z. Elektrochem.*, **48**, 550 (1942).
15. Steinberg, M., "Advances in Nuclear Science and Technology," Vol. 1, pp. 247-333, E. J. Henley and H. Kouts, ed., Academic Press, New York (1962).
16. Swallow, A. J., "Radiation Chemistry of Organic Compounds," Pergamon, Oxford, England (1960).
17. ———, *Brit. Chem. Eng.*, **8**, No. 1, pp. 27-31 (1963).
18. Zimin, A. V., and Z. S. Yegorova, "Collection of Studies in Radiation Chemistry," p. 241, Acad. Sci. USSR, Moscow (1955).

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Optimization of Initial Composition in Adiabatic Equilibrium Gas-Phase Reactions

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Chemical reactions can usually be initiated with components in reasonably arbitrary ratios, limited to some extent by the need to utilize recycle streams, by impurities carried with the reactants, or by the availability of streams of fixed composition arising from an earlier stage in a process. Determination can be made in many cases of the composition of the initial reactant mixture which will realize the greatest equilibrium yield. De Donder and Van Lerberghe (*1*) and Prigogine and Defay (*2*) have proved formally that the components in an isothermal perfect gas reaction should be combined in the stoichiometric ratio in order to attain maximum yield. Pings (*3*) has shown that this result still holds for isothermal reactions carried out in an ideal solution but requires slight modification in dense gases where the interaction terms of the second virial coefficient are significant. In certain cases involving inerts (*4*) carried along with a given reactant, the optimum initial composition may be shifted significantly, with substantial gain in yield. Maximization of economic return (*5*) can also be used as a criterion for selecting optimum feed composition.

This paper presents the determination of the initial distribution of mole fractions required to maximize the equilibrium yield for reactions carried out adiabatically in an ideal solution. Consideration is also given to the selection of an initial composition which will result in the maximum adiabatic equilibrium temperature. In both problems, inerts are assumed absent.

Stoichiometry and yield notation is essentially the same as used before (*4*, *5*). Suppose the reactants are brought together initially at a temperature $T°$. Let $\check{\xi}^0 = 0$. The initial composition is as yet unspecified, its determination being the objective of this derivation. Assume that a single reaction proceeds adiabatically and isobarically until it comes to equilibrium at a temperature T, and a yield $\check{\xi}$. Under isobaric conditions, differential changes in total enthalpy of the system can be expressed in terms of changes in T and ξ as follows (*6*):

$$dH = m\, C_{P,\xi}\, dT + \Delta H_R\, d\xi \tag{1}$$

With the adiabatic-isobaric restraint, if the process is mechanically reversible, the final total enthalpy will equal that of the initial mixture. Therefore, upon integration Equation (1) yields

$$\int_{T^0}^{T} m^0\, C_{P,\xi}\,(T, \xi^0)\; dT + \int_0^{\xi} \Delta H_R\,(\xi, T)\; d\xi = 0 \tag{2}$$

Throughout this paper only ideal solutions are considered. Therefore, the heat of reaction appearing in the second integral above may be removed from within the integral sign. Furthermore, if the system is ideal, the total heat capacity may be represented in terms of the mole fractions and heat capacities of the pure components. Equation (2) may be expressed then as follows:

$$\sum_{1}^{L} y_j^{\,0} <C_{Pj}> [T - T_o] + \Delta H_R\,(T)\check{\xi} = 0 \tag{3}$$

A necessary and sufficient condition for chemical equilibrium is the following (*7*):

$$\sum_{j=1}^{N} \nu_j\, \mu_j / T = 0 \tag{4}$$

There is a normalization restraint on the initial mole fraction distribution, namely that it must sum to unity. This condition of normalization, the condition of equilibrium of Equation (4), and the adiabatic relationship between T and $\check{\xi}$ of Equation (3) represent three restraints that must be simultaneously satisfied in seeking the maximum in any objective function.

MAXIMIZATION OF YIELD

A function $g = g(\check{\xi}, T, y^0_j)$ is assumed of interest. Those values of $\check{\xi}$, T, and $y_j^{\,0}$ are sought which will give a maximum in g, subject to the three restraints discussed in the previous paragraph. In this particular instance, g is identified with the equilibrium yield $g(\check{\xi}, T, y_j^{\,0}) = \check{\xi}$. This problem can be treated rigorously (*8*) by the introduction of three undetermined multipliers and the construction of a set of $L + 3$ simultaneous equations.

These equations may be solved (*3*, *4*, *5*, *9*, *10*, *11*) with the complete elimination of the undetermined multipliers:

$$y_j^{\,0} = \frac{\nu_j}{\nu^{(L)}}\; \frac{1 + \left[\dfrac{\Delta H_R}{RT}\right]^{22} \check{\xi}^2\, C_j(\xi, T, y_j^{\,0})}{1 - \left[\dfrac{\Delta H_R}{RT}\right]^{2} [\check{\xi}/\nu^{(L)}]\, C_j(\xi, T, y_j^{\,0})} \tag{5}$$

$$j = 1, 2 \text{ - - - } L$$

where

$$C_j(\check{\xi}, T, y_j^{\,0}) = \frac{R\,\{[y^0 <C_P>]^{(L)} + \check{\xi}[\nu <C_P>]^{(L)} - [1 + \nu^{(L)}\,\check{\xi}]\, <C_{Pj}>\}}{[y^0 <C_P>]^{(L)}\, \{[y^0\, C_P(T)\,]^{(L)} + \check{\xi}[\nu\, C_P(T)\,]^{(N)}\}} \tag{6}$$

The reader is warned that superscript indexes in parentheses indicate summation over a range and not exponents; for example

$$[y^0 <C_P>]^{(L)} = \sum_{1}^{L} y_j^{\,0} <C_{Pj}> \tag{7}$$

Equation (5) constitutes an implicit solution to the problem, since the right-hand side contains not only the unknown yield and temperature but also the unknown initial mole fraction distribution. However, an explicit first approximation to the desired composition distribution is obtained by substituting the mole fraction distribution corresponding to stoichiometric ratios into the C_j terms on the right-hand side of Equation (6):

$$y_j^{\,0} \simeq \frac{\nu_j}{\nu^{(L)}}\; \frac{1 + \left[\dfrac{\Delta H_R}{RT}\right]^{2} \check{\xi}^2\, [1 + \nu^{(L)}\,\check{\xi}]\, D_j\,(\check{\xi}, T)}{1 - \left[\dfrac{\Delta H_R}{RT}\right]^{2} [\check{\xi}/\nu^{(L)}][1 + \nu^{(L)}\,\check{\xi}]\, D_j(\check{\xi}, T)}$$

$$j = 1, 2 \text{ - - - } L \tag{8}$$

where

$$D_j(\xi, T) = \frac{R\{[\nu <C_P>]^{(L)} - \nu^{(L)} <C_{Pj}>\}\, \nu^{(L)}}{[\nu <C_P>]^{(L)}\, \{[\nu\, C_P(T)\,]^{(L)} + \nu^{(L)}\check{\xi}[\nu\, C_P(T)\,]^{(N)}\}} \tag{9}$$

For small changes, the denominator of the above expression can be expanded in a power series, resulting in the following approximation:

$$y_j^{\,0} \approxeq \frac{\nu_j}{\nu^{(L)}}\; \{1 + [\Delta H_R/RT]^2\, [1 + \nu^{(L)}\,\check{\xi}]^2\, [\check{\xi}/\nu^{(L)}]\, D_j(\check{\xi}, T)\} \tag{10}$$

As a strategy of solution, Equations (3) and (4) might be solved simultaneously for the equilibrium $\check{\xi}$ and T for the case of initial stoichiometric distribution. The solution of that problem can then be substituted into the right-hand side of either Equation (8) or (10) to provide an adjusted value for the mole fraction distribution. The iteration can then be continued by use of Equations (3), (4), and (5). Although this is an iterative scheme, it involves far less groping than the double trial-and-error process of trying to locate the locus of maximum $\check{\xi}$ by merely substituting a sequence of $y_j^{\,0}$ distributions into Equations (3) and (4), followed by iterations at each step to obtain $\check{\xi}$ and T.

Several quantitative observations about the behavior of the solution of Equation (5) can be made. First, from inspection, the correction vanishes if all of the heat capacities are equal. Also, even if the heat capacities are quite different, the correction vanishes for reactions approaching either complete yield or zero yield. Maximum deviations from stoichiometric ratios occur at an intermediate yield, the exact value for which will depend on the parameters of the particular problem but usually will be near $\check{\xi} = 1/3\, \check{\xi}_{\max}$.

MAXIMUM TEMPERATURE

The formal analysis of the preceding section can be used for optimization of variables other than yield. As an example, consider the final equilibrium temperature of the adiabatic reaction, a quantity for which a maximum might indeed be sought in flame temperature problems. The following identification is now made: $g\ (\check{\xi}, T, y_j^0) = T$. The resulting set of simultaneous equations can again be solved, eliminating the undetermined multipliers in the process, and finally yielding the following expression for the initial distribution of mole fractions required to obtain maximum adiabatic temperature:

$$y_j^0 = \frac{\nu_j}{\nu^{(L)}} \; \frac{1 + \theta\check{\xi}^2 E_j\ (\check{\xi}, y_j^0, T)}{1 - \theta\ [\check{\xi}/\nu^{(L)}]\ E_j\ (\check{\xi}, y_j^0, T)} \tag{11}$$

where

$$E_j(\check{\xi}, y_j^0, T) =$$

$$\frac{[y^0{<}C_P{>}]^{(L)} + \check{\xi}[\nu{<}C_P{>}]^{(L)} - [1 + \nu^{(L)}\check{\xi}]\ {<}C_{Pj}{>}}{[y^0{<}C_P{>}]^{(L)}} \tag{12}$$

and

$$\theta = \frac{[\nu^{(N)}]^2}{1 + \nu^{(N)}\check{\xi}} - \sum_1^N \frac{\nu_j^2}{y_j^0 + \nu_j\check{\xi}} \tag{13}$$

An explicit first approximation is again obtained by substituting into the right-hand side of Equation (12) the initial mole fraction distribution corresponding to stoichiometric ratios:

$$y_j^0 \simeq \frac{\nu_j}{\nu^{(L)}}$$

$$\left\{ \frac{1 + [1 - \nu^{(N)}/\nu^{(L)}]\ [\nu^{(L)}\check{\xi}]\ [1 + \nu^{(N)}\check{\xi}]^{-1} J_j(T)}{1 - [1 - \nu^{(N)}/\nu^{(L)}]\ [1 + \nu^{(N)}\xi]^{-1} J_j(T)} \right\} \tag{14}$$

where

$$J_j(T) = \frac{[\nu{<}C_P{>}]^{(L)} - \nu^{(L)}\ {<}C_{Pj}{>}}{[\nu{<}C_P{>}]^{(L)}} \tag{15}$$

For small changes, the denominator of Equation (15) may be expanded in a power series, yielding the following approximation:

$$y_j^0 \simeq \frac{\nu_j}{\nu^{(L)}}$$

$$\{1 + [1 - \nu^{(N)}/\nu^{(L)}]\ [1 + \nu^{(L)}\check{\xi}]\ [1 + \nu^{(N)}\check{\xi}]^{-1} J_j(T)\} \tag{16}$$

As in the case for maximum yield, the corrections to the stoichiometric ratio case disappear if all of the heat capacities are equal. The correction also vanishes if the equilibrium state corresponds to completion. In this case the maximum correction occurs in the limit of zero yield.

DISCUSSION

The analysis leading to Equations (5) and (11) has a generality extending beyond the maximum yield and maximum temperature problems considered in detail above. These techniques are applicable to maximization of any function g which can be characterized in terms of $\check{\xi}$, T, and the J_j^0 distribution. Pings (5) has discussed economic maximization in isothermal systems, in which case g is identified with a profit and is a linear function of $\check{\xi}$ and the y_j^0's. For adiabatic reactions, further dependence of the profit on the equilibrium temperature is quite conceivable.

In conclusion, it may be said that small but nontrivial gains in equilibrium yield can be attained in adiabatic gas-phase reactions by simply adjusting the initial composition of the reactants in a predictable way. The results have been verified by comparison with detailed numerical computations for two real systems, namely the ammonia synthesis and the oxidation of sulfur with pure oxygen.

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NOTATION

C_j = defined by Equation (6)
C_{Pj} = isobaric molal heat capacity of component j
$C_{P,\xi}$ = isobaric, constant composition molal heat capacity of system
D_j = defined by Equation (9)
E_j = defined by Equation (12)
g = an arbitrary function of $\check{\xi}$, T, and y_j^0
H = total enthalpy of the system
ΔH_R = enthalpy of reaction
J_j = defined by Equation (15)
j = index denoting reactant or product
L = total number of reactants
M = total number of products
m = total number of moles in system
m_j = moles of component j
N = $L + M$, total number of components
P = pressure
R = universal gas constant
T = absolute temperature
y_j = mole fraction of component j, m_j/m

Greek Letters

ξ = extent of reaction, moles
$\check{\xi}$ = ξ/m^0
μ_j = molal chemical potential of component j
θ = defined by Equation (13)
ν_j = stoichiometric coefficient of component j

Superscripts

(L) = summation over range 1 to L
(N) = summation over range 1 to N
0 = condition in original mixture

Subscripts

j = component j

LITERATURE CITED

1. De Donder, Th., and G. Van Lerberghe, *Bull. Ac. Roy. Belg.* (*Cl. Sc.*), **12**, No. 5, p. 151 (1926).
2. Prigogine, I., R. Defay, and D. H. Everett, "Chemical Thermodynamics," p. 134, Longmans Green & Co., London, England (1954).
3. Pings, C. J., *Ind. Eng. Chem. Fundamentals*, **2**, 244 (1963).
4. *Ibid.*, p. 321.
5. ———, *Chem. Eng. Progr.*, **59**, No. 12, p. 90 (1963).
6. Prigogine, I., R. Defay, and D. H. Everett, "Chemical Thermodynamics," p. 24, Longmans Green & Co., London, England (1954).
7. *Ibid.*, p. 69.
8. Franklin, Philip, "A Treatise on Advanced Calculus," p. 353, Wiley, New York (1940).
9. Pings, C. J., *Chem. Eng. Sci.*, **16**, 181 (1961).
10. *Ibid.*, **17**, 861 (1962).
11. *Ibid.*, **18**, 671 (1963).

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