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Use of an ensemble intermediate between the generalized ensemble and the isothermal–isobaric ensemble to calculate the equilibrium distribution of hydrocarbons in homologous series

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The ensemble first introduced by Stockmayer to study the relation between light scattering and composition fluctuations of solutions provides the basis for calculating equilibrium mole fractions of isomer groups in homologous series. The number of molecules of one component in a system at a particular temperature and pressure is held constant, and another component is provided through a semipermeable membrane at a specified chemical potential. The equilibrium alkylation of benzene may be calculated by fixing the number of molecules of benzene in the system and providing ethylene through a semipermeable membrane. A catalyst for the formation of all possible isomers of all possible alkyl benzenes, or some subset of these species, is assumed to be present. The advantage of using this approach is that exponential distributions are obtained that are a function of the ethylene partial pressure for ideal mixtures of perfect gases. The Gibbs energy of formation obtained from the Stockmayer ensemble can be used to calculate the equilibrium constant of a reaction written in terms of isomer groups.

INTRODUCTION

The calculation of equilibrium distributions of species in complex organic mixtures is complicated by the need to conserve atoms, the very large numbers of species, and lack of data. General equilibrium programs are available^{1,2} that can be used to compute equilibrium compositions for defined sets of species, but the results are numbers rather than analytic functions and it is difficult to get insight as to what determined the equilibrium state. This may be compared with the approach of statistical mechanics that uses pistons, reservoirs, and semipermeable membranes and yields exponential distributions. Since chemical equilibrium is usually studied at constant temperature and pressure, the isothermal–isobaric ensemble provides the most direct route to the Gibbs energy. The generalized ensemble, introduced by Guggenheim³ and Fowler and Guggenheim,⁴ applies to a system in thermal, mechanical, and material contact with its surroundings. However, it is the ensemble, intermediate between these two, that was introduced by Stockmayer,⁵ that provides the basis for calculating the equilibrium distribution in a system in material contact with a reservoir containing one or more reactants. These various ensembles have been carefully described by Hill.^{6,7} The partition function $\Gamma(N_1, P, T, \mu_2)$ for this ensemble may be written in terms of the partition function $\Delta(N_1, P, T)$ for the isothermal–isobaric ensemble as follows:

$$\Gamma(N_1, P, T, \mu_2) = e^{-N_1 \mu_1 / kT} = \sum_{N_2 \geq 0} \Delta_{N_2}(N_1, P, T) e^{N_2 \mu_2 / kT}. \quad (1)$$

The Stockmayer partition function $\Gamma(N_1, P, T, \mu_2)$ yields the chemical potential μ_1 of the component restricted to the system by the semipermeable membrane. Before applying this distribution function, the thermodynamics of equilibria within a homologous series will be discussed.

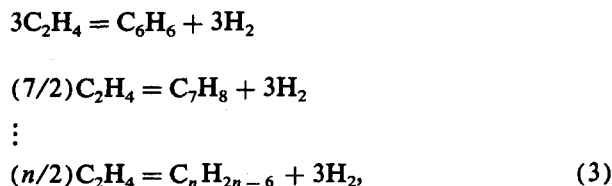
THERMODYNAMICS OF EQUILIBRIA WITHIN A HOMOLOGOUS SERIES

As a simplification a homologous series may be considered to be made up of a series of isomer groups, successive groups differing by CH_2 . The standard Gibbs energy of formation $\Delta_f G^0(I)$ of an isomer group can be calculated using^{1,8}

$$\Delta_f G^0(I) = -RT \ln \left(\sum_{i=1}^{N_I} e^{-\Delta_f G_i^0 / RT} \right), \quad (2)$$

where N_I is the number of isomers in an isomer group and $\Delta_f G_i^0$ is the standard Gibbs energy of formation of the i th isomer. The equilibrium mole fractions of successive isomer groups can be calculated at various H/C ratios using a general equilibrium program. Alberty⁹ showed that the equilibrium distribution may also be calculated as a function of the partial pressure of ethylene. This has the advantage that homologous series of hydrocarbons that are in equilibrium with the same partial pressure of ethylene are in equilibrium with each other. Alberty and Oppenheim¹⁰ showed that when the standard Gibbs energies of the isomer groups are a linear function of carbon number, as is found experimentally after the first several members of a homologous series, the equilibrium distribution may be expressed by an analytic function of the partial pressure of the ethylene. This has the advantage that the mean carbon number and the carbon number contributing the largest weight fraction for given conditions can be calculated without calculating the whole distribution using a general equilibrium program.

The form of the equations for calculating the equilibrium mole fractions for successive isomer groups may be illustrated by considering the alkylation of benzene.⁹ For this purpose the formation reactions of the isomer groups are written as follows:



where n is an integer. When comparing different homologous series it is better to write the formation reactions in this way, rather than in the way used in previous papers.^{9,10} Assuming an ideal mixture of perfect gases, the standard Gibbs energy of formation $\Delta_f G^\circ(I, \text{C}_n\text{H}_{2n-6})$ of an isomer group at a particular partial pressure of ethylene is given by

$$\begin{aligned}
 \Delta_f G^\circ[\text{C}_n\text{H}_{2n-6}(I), P_{\text{C}_2\text{H}_4}] \\
 = \Delta_f G^\circ[\text{C}_n\text{H}_{2n-6}(I)] \\
 - (n/2)(\Delta_f G^\circ_{\text{C}_2\text{H}_4} + RT \ln P_{\text{C}_2\text{H}_4}),
 \end{aligned} \quad (4)$$

where $\Delta_f G^\circ[\text{C}_n\text{H}_{2n-6}(I)]$ is calculated using Eq. (2). The symbol P will be taken to represent the ratio of the actual pressure to the standard-state pressure of 1 bar. At a fixed partial pressure of ethylene, the successive isomer groups within a homologous series become pseudoisomers in the sense that their relative mole fractions are a function of temperature only. Thus the standard Gibbs energy of formation of the benzene homologous series group is given by the following analog of Eq. (2):

$$\Delta_f G^\circ(\text{HSG}) = -RT \ln \left(\sum_{n=6}^{\infty} \exp\{-\Delta_f G^\circ[\text{C}_n\text{H}_{2n-6}(I), P_{\text{C}_2\text{H}_4}]/RT\} \right). \quad (5)$$

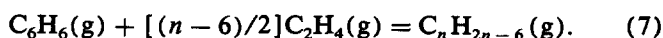
The equilibrium mole fractions of successive isomer groups are then given by

$$\begin{aligned}
 y_n &= \frac{\exp\{-\Delta_f G^\circ[\text{C}_n\text{H}_{2n-6}(I), P_{\text{C}_2\text{H}_4}]/RT\}}{\exp[-\Delta_f G^\circ(\text{HSG})/RT]} \\
 &= \frac{\exp\{-\Delta_f G^\circ[\text{C}_n\text{H}_{2n-6}(I)]/RT\} \exp\{[(n/2)\mu_{\text{C}_2\text{H}_4}]/RT\}}{\exp[-\Delta_f G^\circ(\text{HSG})/RT]},
 \end{aligned} \quad (6)$$

where $\mu_{\text{C}_2\text{H}_4} = \Delta_f G^\circ_{\text{C}_2\text{H}_4} + RT \ln P_{\text{C}_2\text{H}_4}$ and $n = 6, 7, \dots$. Thus the equilibrium mole fraction depends on two factors: The first is determined by the molecular properties of the isomers in the groups, and the second is determined by the chemical potential of ethylene that is assumed to be available through a semipermeable membrane. The distribution is, of course, independent of whether it is produced by ethylene or simply by disproportionation within the alkylbenzenes.

STATISTICAL MECHANICS OF EQUILIBRIA WITHIN A HOMOLOGOUS SERIES

The ensemble used here is intermediate between the generalized ensemble and the isothermal-isobaric ensemble. The system of interest is in a piston, so that it can be maintained at constant pressure, and it is in contact with a heat reservoir, so that it can be maintained at constant temperature. The system is also in contact with a reservoir of ethylene through a semipermeable membrane, so that ethylene is available at a constant chemical potential. As a specific example, the system initially contains benzene vapor, and reaction with ethylene produces all possible alkylbenzenes and their isomers. A perfect catalyst is assumed to be present, but the catalyst and the ethylene are excluded from the calculation of the most probable distribution of mole fractions. The system is assumed to be an ideal mixture of perfect gases. The membrane is assumed to be permeable only to ethylene so that the number N_1 of molecules in the system is fixed. The number of molecules in the system is fixed because the perfect catalyst only catalyzes the following reaction:



In writing the partition function for this ensemble we have to consider all possible isomer groups for the alkylbenzenes; that is, n goes from 6 to infinity. To simplify the dis-

cussion we will treat isomer groups as if they were single molecular species. This is possible because they behave thermodynamically like single molecular species at a constant temperature in an ideal mixture of perfect gases in the presence of a catalyst for reaction (7). From a statistical mechanical viewpoint, the partition function for an isomer group consists of a sum of terms for the various isomers.

In the partition function introduced by Stockmayer,⁵ the successive terms are for $N_2 = 0, 1, 2, \dots$. In applying this partition function to the alkylation of benzene, N_2 corresponds to the number of CH_2 groups added to benzene to make a particular isomer group. Thus $N_2 = 3, 7/2, 4, 9/2, \dots$. The first several terms in the partition function are therefore given by

$$\begin{aligned}
 \Gamma(N_1, P, T, \mu_2) \\
 = \Delta_3(N_1, P, T) e^{3\mu_2/kT} + \Delta_{7/2}(N_1, P, T) e^{7\mu_2/2kT} \\
 + \Delta_4(N_1, P, T) e^{4\mu_2/kT} + \Delta_{9/2}(N_1, P, T) e^{9\mu_2/2kT} + \dots,
 \end{aligned} \quad (8)$$

where Δ_3 is the isothermal-isobaric partition function for benzene, $\Delta_{7/2}$ is for toluene, and Δ_4 is for the isomer group made up of the xylenes and ethylbenzene. This equation may be written in terms of n , the number of carbon atoms of the molecules of an isomer group, as follows:

$$\begin{aligned}
 \Gamma(N_1, P, T, \mu_2) &= \Delta_6 e^{6\mu_2/2kT} + \Delta_7 e^{7\mu_2/2kT} + \Delta_8 e^{8\mu_2/2kT} \\
 &+ \dots + \Delta_n e^{(n/2)\mu_2/kT} + \dots.
 \end{aligned} \quad (9)$$

The isothermal-isobaric partition function Δ yields the Gibbs energy for an isomer group directly

$$\Delta_n = e^{-NG_n/kT}, \quad (10)$$

where N is the number of molecules and G_n is the Gibbs energy per molecule for the isomer group with n carbon

atoms. Since we are considering the property of a pure component we might as well consider one mole and write this equation in terms of the standard molar Gibbs energy of formation:

$$\Delta_n = e^{-\Delta_f G_n^0/RT} \quad (11)$$

This has the effect of restricting the calculation to the standard-state pressure, but that is all right since the disproportionation equilibria are independent of pressure for ideal mixtures of perfect gases. The Gibbs energy of formation in Eq. (11) is with respect to graphite and molecular hydrogen, but this cancels in any use of the partition function to calculate the equilibrium mole fraction of a particular isomer group. Thus Eq. (9) becomes

$$\begin{aligned} \Gamma(N_1, P, T, \mu_2) = & e^{-\Delta_f G^0/RT} e^{6\mu_2/2kT} + e^{-\Delta_f G^0/RT} e^{7\mu_2/2RT} \\ & + e^{-\Delta_f G^0/RT} e^{8\mu_2/2RT} + \dots \\ & + e^{-\Delta_f G^0/RT} e^{(n/2)\mu_2/RT} + \dots \end{aligned} \quad (12)$$

The equilibrium mole fraction of the n th isomer group within a homologous series group is given by

$$y_n = \frac{e^{-\Delta_f G_n^0/RT} e^{(n/2)\mu_2/RT}}{\Gamma(N_1, P, T, \mu_2)} = \frac{e^{-\Delta_f G_n^0/RT} e^{(n/2)\mu_2/RT}}{e^{-\Delta_f G^0/RT}} \quad (13)$$

This equation is the same as Eq. (6). This shows that $\exp[-\Delta_f G^*(\text{HSG})/RT]$, defined in Eq. (5), is the partition function for this particular ensemble that is intermediate between the generalized ensemble and the isothermal-isobaric ensemble.

USE OF THE STANDARD GIBBS ENERGY OF FORMATION OF A HOMOLOGOUS SERIES GROUP AT A PARTICULAR $P_{C_2H_4}$ TO CALCULATE EQUILIBRIUM CONSTANTS

The identification of $\Delta_f G^*(\text{HSG})$ in Eq. (5) and $\Delta_f G^0$ in Eq. (13) as the same quantity (provided the same reference states are used) and as the standard Gibbs energy of formation of a homologous series group at a particular partial pressure of ethylene suggests that it may also be used to calculate the equilibrium constant for a chemical reaction written in terms of homologous series groups. This may be illustrated using the conversion of methanol to gasoline with a zeolite catalyst.¹¹ The passage of methanol through a zeolite catalyst at about 700 K produces a gasoline containing alkanes, alkenes, and alkylbenzenes. It also contains alkylcyclopentanes and alkylcyclohexanes, but since these substances have formulas $C_q H_{2q}$, where $q = 5, 6, \dots$, they can be considered part of the alkene isomer groups and alkene homologous series. In the conversion of methanol to gasoline using a zeolite catalyst, alkenes are formed rather quickly and polymerize to an equilibrium distribution. Thus as a first approximation the important reaction for the conversion of methanol to gasoline is

$$\frac{1}{Q} C_Q H_{2Q} = \frac{3}{3M+N} C_M H_{2M+2} + \frac{1}{3M+N} C_N H_{2N-6} \quad (14)$$

In this chemical equation the molecular formulas represent average compositions of equilibrium mixtures of alkenes ($C_Q H_{2Q}$), alkanes ($C_M H_{2M+2}$), and alkylbenzenes ($C_N H_{2N-6}$) at a particular partial pressure of ethylene. Since Q , M , and N are continuous functions of $P_{C_2H_4}$, the stoichiometric coefficients are also continuous functions of $P_{C_2H_4}$. We are concerned here with the question as to whether the value of the equilibrium constant can be calculated using $\Delta_f G^*(\text{HSG})$ values for the various reactants and products. Following the pattern of Eq. (3), we will write the formation reactions for the various reactants as

$$(Q/2) C_2 H_4 = C_Q H_{2Q}, \quad 2 < Q < \infty, \quad (15)$$

$$(M/2) C_2 H_4 + H_2 = C_M H_{2M+2}, \quad 1 < M < \infty, \quad (16)$$

$$(N/2) C_2 H_4 = C_N H_{2N-6}, \quad 6 < N < \infty. \quad (17)$$

The change in Gibbs energy for reaction (14) at a specified partial pressure of ethylene and $P_{H_2} = 1$ bar is given by

$$\begin{aligned} \Delta G^* = & \frac{3}{3M+N} \Delta_f G^*(C_M H_{2M+2}) \\ & + \frac{1}{3M+N} \Delta_f G^*(C_N H_{2N-6}) \\ & - \frac{1}{Q} \Delta_f G^*(C_Q H_{2Q}). \end{aligned} \quad (18)$$

The left-hand side of this equation is equal to $-RT \ln K$, where K is the equilibrium constant at a particular T and $P_{C_2H_4}$. The $\Delta_f G^*$ values on the right-hand side of the equation may be replaced by $-RT \ln$ of the equilibrium constant for the corresponding formation reaction to obtain

$$\begin{aligned} \ln K = & \frac{3}{3M+N} \ln \frac{P_{C_M H_{2M+2}}}{P_{C_2 H_4}^{M/2} P_{H_2}} + \frac{1}{3M+N} \ln \frac{P_{C_N H_{2N-6}} P_{H_2}^3}{P_{C_2 H_4}^{N/2}} \\ & - \frac{1}{Q} \ln \frac{P_{C_Q H_{2Q}}}{P_{C_2 H_4}^{Q/2}}. \end{aligned} \quad (19)$$

Thus we obtain an expression for the equilibrium constant of reaction (14) that is written in terms of partial pressures homologous series

$$K = \frac{P_{C_M H_{2M+2}}^{3/(3M+N)} P_{C_N H_{2N-6}}^{1/(3M+N)}}{P_{C_Q H_{2Q}}^{1/Q}} \quad (20)$$

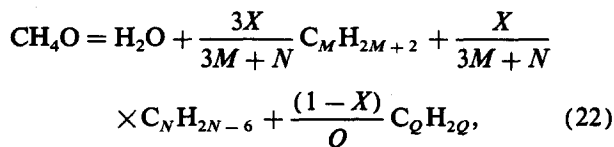
This shows that $\Delta_f G^*(\text{HSG})$ can be used like other standard Gibbs energies of formation in calculating equilibrium constants. Use of the usual thermodynamic derivatives with Eq. (5) yields expressions for $\Delta_f H^*(\text{HSG})$, $\Delta_f S^*(\text{HSG})$, and $\Delta_f C_p^*(\text{HSG})$. These quantities are, of course, all functions of $P_{C_2H_4}$ as well as the temperature. Alberty and Oppenheim¹⁰ have shown that when the standard Gibbs energies of formation of isomer groups in a homologous series are a linear function of carbon number, the series in Eq. (5) may be summed to obtain a relatively simple function of $P_{C_2H_4}$ at a constant temperature.

There is another way of formulating the conversion of methanol to gasoline that further extends the concept of a balanced chemical equation. If a general equilibrium program² is used to calculate the equilibrium composition for a mixture of alkanes, alkylbenzenes, and alkenes with a gross composition equal to that of methanol, it is found that the

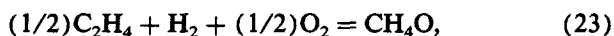
following reaction goes essentially to completion:



In the production of gasoline from methanol the conversion is not allowed to go this far. At earlier stages in the conversion, alkenes are present and alkylate the alkanes and alkylbenzenes. At intermediate times the stoichiometry of the reaction can be represented by



where X is the extent of conversion to alkanes and alkylbenzenes. At a particular value of X at a given pressure and temperature there will be a certain equilibrium distribution of alkenes. We can think of the partial pressure of ethylene as determining the equilibrium distributions of the various alkane and alkylbenzene isomer groups. Thus if the alkylation of alkanes, alkylbenzenes, and alkenes remains at equilibrium, Eq. (22) represents compositions at various extents of conversion X from $X = 0$ to $X = 1$. At $X = 0$, alkenes are the only organic products, and at $X = 1$ the conversion is represented by Eq. (21). As in the case of reaction (14), the equilibrium constant of reaction (22) may be calculated using Gibbs energies of formation of homologous series groups. To derive the expression for the equilibrium constant, we need to add two formation reactions to those given in reactions (15) to (17):



The "standard" Gibbs energy change for reaction (22) is given by

$$\begin{aligned} \Delta_f G^* = & \Delta_f G^0(\text{H}_2\text{O}) + \frac{3X}{3M+N} \Delta_f G^*(\text{C}_M\text{H}_{2M+2}) \\ & + \frac{X}{3M+N} \Delta_f G^*(\text{C}_N\text{H}_{2N-6}) \\ & + \frac{(1-X)}{Q} \Delta_f G^*(\text{C}_Q\text{H}_{2Q}) - \Delta_f G^*(\text{CH}_4\text{O}). \end{aligned} \quad (25)$$

In this case standard means formed from $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ at 1 bar and ethylene at a specified value of $P_{\text{C}_2\text{H}_4}$. The only substance with the usual reference state is H_2O . When the left-hand side of this equation is replaced with $-RT \ln K$ and the equilibrium expressions for the formation reactions are introduced on the right, we obtain

$$\begin{aligned} \ln K = & \ln \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}} + \frac{3X}{(3M+N)} \ln \frac{P_{\text{C}_M\text{H}_{2M+2}}}{P_{\text{C}_2\text{H}_4}^{M/2} P_{\text{H}_2}} \\ & + \frac{X}{(3M+N)} \ln \frac{P_{\text{C}_N\text{H}_{2N-6}} P_{\text{H}_2}^3}{P_{\text{C}_2\text{H}_4}^{N/2}} \\ & + \frac{(1-X)}{Q} \ln \frac{P_{\text{C}_Q\text{H}_{2Q}}}{P_{\text{C}_2\text{H}_4}^{Q/2}} - \ln \frac{P_{\text{CH}_4\text{O}}}{P_{\text{C}_2\text{H}_4}^{1/2} P_{\text{H}_2} P_{\text{O}_2}^{1/2}}, \end{aligned} \quad (26)$$

so that

$$K = P_{\text{H}_2\text{O}} P_{\text{C}_M\text{H}_{2M+2}}^{3X/(3M+N)} P_{\text{C}_N\text{H}_{2N-6}}^{X/(3M+N)} P_{\text{C}_Q\text{H}_{2Q}}^{(1-X)/Q} / P_{\text{CH}_4\text{O}}. \quad (27)$$

This expression for the equilibrium constant applies to reaction (22) at a particular extent of reaction X . The ethylene used in calculating Gibbs energies of homologous series groups is formed in the reaction.

Before discussing the calculation of the equilibrium composition at various extents of reaction X , it should be observed that according to the phase rule there are two degrees of freedom if the initial composition is fixed at CH_4O . It is convenient to take these as the pressure and temperature. It is even more convenient to take the sum of the partial pressures of the organic components since the dehydration reaction goes essentially to completion.

The equilibrium composition at any extent of conversion can be calculated as follows: At a given partial pressure of ethylene the equilibrium mole fraction of ethylene and of each of the successive alkene isomer groups within the alkene homologous series group can be calculated using the alkene analog of Eq. (6). The partial pressure of the alkene isomer group can then be calculated using

$$P_{\text{C}_Q\text{H}_{2Q}} = P_{\text{C}_2\text{H}_4} / y_2, \quad (28)$$

where y_2 is the equilibrium mole fraction of ethylene in the alkene homologous series. Since the total pressure is fixed, the sum of the equilibrium partial pressures of the alkanes and alkylbenzenes is readily calculated. Since the amounts of these homologous series have a 3:1 ratio, the equilibrium mole fractions of these homologous series are readily calculated. The equilibrium mole fractions of the alkylbenzene isomer groups can be calculated using Eq. (6), and the equilibrium mole fractions of the alkane isomer groups can be calculated with an analogous equation. The equilibrium mole fractions of individual species within each isomer group can be calculated using their standard Gibbs energies of formation and Eq. (2).

The calculation of the composition at various extents of reaction for the conversion of methanol to gasoline is an example of the implementation of the rapid-equilibrium assumption of chemical kinetics on a computer.

The standard enthalpy changes for reactions (14) and (22) may be calculated using $\Delta_f H^*(\text{HSG})$, which may be derived from Eq. (5) by differentiating with respect to $1/T$:

$$\Delta_f H^*(\text{HSG}) = \left\{ \frac{\partial [\Delta_f G^*(\text{HSG})/T]}{\partial (1/T)} \right\}_{P, P_{\text{C}_2\text{H}_4}}. \quad (29)$$

DISCUSSION

The derivation of the expression for the equilibrium mole fraction of an isomer group within a homologous series group using statistical mechanics has clarified the significance of the Gibbs energy of formation $\Delta_f G^*(\text{HSG})$ of a homologous series group at a specified partial pressure of ethylene. This approach to calculations of equilibrium compositions in complicated organic systems can be generalized both with respect to species that are retained in the system by the semipermeable membrane and with respect to species that can pass through the membrane. An example of a sys-

tem with alkanes, alkylbenzenes, and alkenes, other than ethylene, retained within the system has been discussed. As an example of the second type of extension, several elements may be admitted to a system through a semipermeable membrane.

An advantage of this procedure for making calculations on complicated organic systems is that it helps visualize what is happening. For example, the degree of alkylation increases as $P_{C_2H_4}$ in the reservoir is increased. However, the equilibrium distribution of alkylbenzenes, e.g., is independent of whether ethylene is actually present or not. That is, the same distribution of isomer groups is obtained at the H/C ratio for the alkylbenzenes with a general equilibrium program.¹⁰

Another advantage of this procedure is that where increments in $\Delta_f G^0(I)$ for successive isomer groups in a homogeneous series are constant, the equilibrium distribution of isomer groups can be expressed as an analytic function of the carbon number.¹⁰ This makes it possible to calculate the mean carbon number and the carbon number contributing the largest weight fraction for given conditions, without calculating the whole distribution using a general equilibrium program.

Catalyst selectivity can be provided for in calculations

of this type by excluding isomers which are excluded by the catalyst.

ACKNOWLEDGMENTS

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