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SUMMARY

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A number of homogeneous stoichiometric chemical reactions were investigated to determine the particular manner in which the affinity varied with time as these reactions proceeded. The actual kinetic data were solicited from investigators whose results had appeared in the literature. The study included both gas-phase and liquid-phase reactions.

For more than two-thirds of the 113 reactions investigated, a single empirical relation was sufficient to describe the manner in which the affinity varied with time. The correlation of the observed reactions by this relation was at least equal to that attainable by use of the classical empirical rate equations. author

INTRODUCTION

Irreversible phenomena, such as chemical reactions, are characterized thermodynamically as positive producers of entropy. In an isothermal system in which the only irreversible phenomenon is a chemical reaction, De Donder (ref. 1) showed that the production of entropy per unit time is Av/T when

$$\frac{Av}{T} > 0 \tag{1}$$

where v is the rate of reaction; T, the absolute temperature; and A, the affinity. For the chemical reaction

$$\sum_i \nu_i M_i = 0 \tag{2}$$

where ν_i is the stoichiometric coefficient and M_i is the molecular weight of component i, the affinity can be equated to the chemical potentials μ_i (ref. 2) by

$$A = -\sum_i \nu_i \mu_i \tag{3}$$

The stoichiometric coefficients have a positive value when the component is a product and a negative value when it is a reactant. Equation (3) indicates that the affinity can be considered a measure of the thermodynamic force or tendency for reaction.

The kinetic behavior of a chemical reaction proceeding toward equilibrium in a closed isothermal system can be related to the thermodynamic force or affinity, customarily by a simple linear phenomenological relation between the reaction rate and the force. Such a relation is similar to that used to represent transport phenomena, such as diffusion and thermal conductivity. In the case of chemical reactions, the linear relation takes the form

$$v = LA \tag{4}$$

where L is the linear phenomenological coefficient.

Equation (4), introduced ad hoc into the phenomenological theories of irreversible thermodynamics for the purpose of theoretically interpreting chemical reactions, is inadequate in describing the kinetic behavior of most observed reactions (ref. 3). Although Prigogine, Outer, and Herbo (ref. 4) showed that equation (4) can describe kinetic behavior for a reaction in a flow system for which the affinity is assumed constant, such a reaction does not proceed towards equilibrium in a closed system.

For the aforementioned reason, the phenomenological approach is not used in this study, the object and scope of which is to examine the affinity as a direct kinetic variable for chemical reactions proceeding towards equilibrium.

The actual kinetic data with which this study was carried out were solicited from investigators whose results had been reported in the literature. The use of these data is gratefully acknowledged.

SYMBOLS

A	affinity of reacting system
A^o	affinity of reacting system when components are in their reference state
A_r	affinity rate coefficient

a_i	activity of component i
K	thermodynamic equilibrium constant
L	linear phenomenological coefficient
M_i	molecular weight of component i
Q	activity quotient
Q_{eq}	activity quotient at equilibrium
R	gas constant
T	absolute temperature
t	elapsed time
t_K	elapsed time at which $Q = K$
t_1	elapsed time at which $Q = 1$
v	rate of reaction
ζ_Q, ζ_t	extent of reaction
μ_i	chemical potential of component i
μ_i^o	chemical potential of component i in reference state
ν_i	stoichiometric coefficient of component i

THERMODYNAMIC CONSIDERATIONS AND METHOD OF APPROACH

The variation of the affinity with time is the primary kinetic variable treated herein. Consider a homogeneous chemical reaction proceeding toward equilibrium in a closed isothermal system. Classically, the chemical potential μ_i of component i in any arbitrary state can be related to its chemical potential μ_i^o in some reference state by an equation of the form

$$\nu_i \mu_i = \nu_i \mu_i^o + RT \ln(a_i)^{\nu_i} \tag{5}$$

where R is the gas constant and a_i is the activity of component i in the chosen arbitrary state.

Equation (5) can be expressed in terms of affinities by combining it with equation (3):

$$A = A^o - RT \sum_i \ln(a_i)^{\nu_i} \tag{6}$$

where A^o is the affinity of the reacting system when the components are in their reference state and is a function only of temperature. If the activity quotient Q is defined as

$$Q = \prod_i (a_i)^{\nu_i} \tag{7}$$

equation (6) can be expressed as

$$A = A^o - RT \ln Q \tag{8}$$

Because the affinity is positive for an irreversible reaction (relation (1)) and is zero at equilibrium (entropy production ceases), the affinity must decrease toward zero for a reaction proceeding towards equilibrium.

$$\left(\frac{\partial A}{\partial t}\right)_T < 0 \tag{9}$$

Because no theoretical model is available to describe the rate of the aforementioned process, a relation will be introduced ad hoc to resolve the inequality expressed in relation (9). The particular form of the relation was determined from an empirical analysis of more than 100 chemical reactions. The study was restricted to homogeneous reactions that occurred in closed isothermal systems.

Relation (9) can be expressed in terms of experimentally measurable quantities by substituting the activity quotient term of equation (8) for the affinity:

$$RT\left(\frac{\partial \ln Q}{\partial t}\right)_T > 0 \tag{10}$$

Relation (10) is amenable to empirical analysis.

EMPIRICAL ANALYSIS

Determining empirically the particular manner in which the activity quotient term of relation (10) varies as a reaction proceeds requires the calculation of the activity quotient at various time intervals. Because the activity quotient is defined in terms of the stoichiometry of a particular reaction, the empirical analysis of various reactions in terms of relation (10) must be restricted to those reactions that can be represented by a

single stoichiometric equation. The actual reaction may proceed in multiple steps and involve intermediate species, but the products must appear and the reactants disappear according to the stoichiometry of the overall equation.

Although the activity quotient is experimentally measurable, virtually all kinetic data are in terms of partial pressures or concentrations. The reactions to be analyzed must thus not only meet the stoichiometric requirements but must occur at low pressures or in dilute solutions, so that the partial pressures or concentrations of reacting species approximate their activities.

For the majority of reactions considered, the activity quotient term of relation (10) could be related with a high degree of correlation to the elapsed time by an expression of the form

$$RT\left(\frac{\partial \ln Q}{\partial t}\right)_T \propto \frac{1}{t} + C_1 \tag{11}$$

where C_1 is a constant, the value of which is associated with the particular reaction investigated. From the condition at equilibrium that the overall rate of reaction is zero, the constant C_1 can be defined in terms of a quantity t_K, the elapsed time to attain equilibrium:

$$C_1 = -\frac{1}{t_K} \tag{12}$$

The concept of t_K as a finite quantity will be discussed subsequently in more detail.

Relation (11) can be expressed as an equation by the introduction of a constant of proportionality A_r:

$$RT\left(\frac{\partial \ln Q}{\partial t}\right)_T = A_r\left(\frac{1}{t} - \frac{1}{t_K}\right) \tag{13}$$

Integrating yields

$$\ln Q = \frac{A_r}{RT}\left(\ln t - \frac{t}{t_K}\right) + C_2 \tag{14}$$

where C_2 is a constant of integration.

TABLE I. - KINETIC AND THERMODYNAMIC PARAMETERS ASSOCIATED WITH SOME HOMOGENEOUS STOICHIOMETRIC REACTIONS

Reaction number	Reaction	Initial pressure, torr		Initial concentration, molarity		Temperature, ^{o}K	Activity rate coefficient, A_r, cal/mole	ln t_K (a)	ln K	Reference	
		First reactant	Second reactant	First reactant	Second reactant					Thermodynamic data	Kinetic data
1a	Dehydrogenation of isobutane by	200.3	9.67	------	------	525.1	3170	10.6	-6.14	5	6
1b	iodine: $C_4H_{10} + I_2 \rightarrow 2HI + C_4H_8$	275.4	3.89	------	------	525.7	3030	10.7	-6.10	↓	↓
1c		206.5	7.5	------	------	551.9	3280	9.27	-4.87		
1d		121.2	14.8	------	------	552.5	3350	9.36	-4.85		
1e		158.7	4.32	------	------	552.5	2850	9.77	-4.85		
1f		131.9	8.37	------	------	582.7	2920	8.37	-3.66		
1g		136.7	3.56	------	------	582.9	3000	8.63	-3.64		
1h		168.8	5.95	------	------	582.7	3020	8.50	-3.67		
2a	Conversion of	250	-----	------	------	490.7	1020	8.83	-0.26	7	7
2b	ethylidenecyclopropane to	250	-----	------	------	507.0	1020	8.83	-.24	↓	↓
2c	2-methylmethylenecyclopropane	[b]250	-----	------	------	507.0	1120	8.91	.24		
3a	Decomposition of hydrogen	9.6	19.2	------	------	704.7	4660	23.7	51.8	8	9
3b	peroxide vapor in helium:	↓	↓	------	------	712.8	4590	23.5	51.4	↓	↓
3c	$2H_2O_2 \rightarrow 2H_2O + O_2$			------	------	721.6	4830	22.3	51.0		
3d				------	------	731.6	4970	21.6	50.5		
3e			↓	------	------	741.6	5060	21.0	50.0		
3f			48.0	------	------	704.7	4490	24.9	51.8		
3g			↓	------	------	712.8	4590	23.3	51.4		
3h				------	------	721.6	4900	21.9	51.0		
3i				------	------	731.6	5020	21.3	50.5		
3j		↓	↓	------	------	741.7	5120	20.6	50.0	↓	↓
4a	Reaction of styrene with iodine in	------	-----	0.3472	0.2032	295	294	5.59	0.095	10	10
4b	carbon tetrachloride:	------	-----	↓	.00053	295	422	6.44	↓	↓	↓
4c	$C_6H_5CHCH_2 + I_2 \rightarrow C_6H_5CHI_2CH_2$	------	-----		.00405	295	600	4.95			
4d		------	-----		.000203	295	566	5.55			

[a]Where t_K is in seconds.

[b]Reverse reaction.

At equilibrium, the activity quotient is expressible in terms of the equilibrium concentrations of the reacting species:

$$Q_{eq} = \prod_i (a_i)_{eq}^{\nu_i} \tag{15}$$

Because this is the same form in which the equilibrium constant K is expressed,

$$Q_{eq} = K \tag{16}$$

Thus, both the composition and the time variables of equation (14) have finite limits:

$$0 \leq Q \leq K \quad \text{and} \quad 0 \leq t \leq t_K \tag{17}$$

They can therefore be expressed in terms of a dimensionless "extent of reaction," defined as follows:

$$\zeta_Q = \frac{Q}{K} \quad \text{and} \quad \zeta_t = \frac{t}{t_K} \tag{18}$$

where $0 \leq \zeta_{Q,t} \leq 1$. This representation permits the kinetic data of all the reactions correlated by equation (14) to be expressed by the same parameters.

From the condition at equilibrium that $\zeta_Q = \zeta_t = 1$, equation (14) can be expressed as

$$\ln \zeta_Q = \frac{A_r}{RT} (\ln \zeta_t - \zeta_t + 1) \tag{19}$$

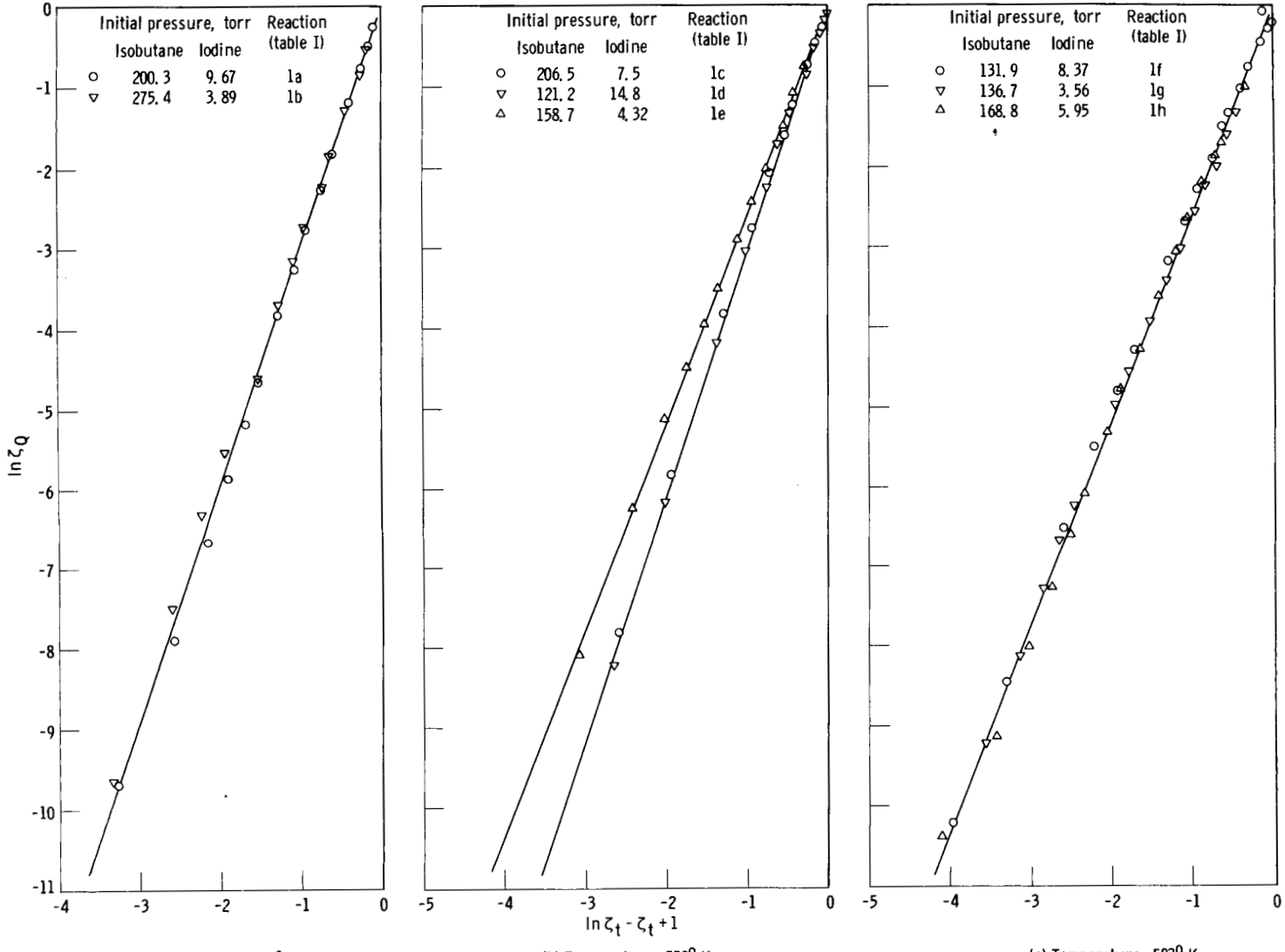
For the cases in which the equilibrium constant was attainable from the literature, the experimental time-concentration data were expressed in terms of the extent of reaction. A correlation was then made according to equation (19) by a least-squares determination with the aid of an electronic data processing machine. The value of t_K for each reaction was generated internally by the requirement that the line of regression must pass through the origin in accordance with equation (19). The value of A_r was then calculated from the slope. The values of the parameters A_r and t_K for four homogeneous stoichiometric reactions are listed in table I.

Unfortunately, thermodynamic equilibrium data are not available for the great majority of reactions investigated. Use can still be made of equation (14), however, if the

TABLE II. - VALUE OF PARAMETERS A_r AND $\ln t_1$ ASSOCIATED WITH VARIOUS CHEMICAL REACTIONS UNDER CONDITIONS CITED

Reaction number	Reaction	Solvent or diluent	Initial pressure, torr	Initial concentration, molarity		Reaction order	Temperature, °K	Activity rate coefficient, A_r, cal/mole	$\ln t_1$ (a)	Reference
				First reactant	Second reactant					
1	Decomposition of di-tert-butyl peroxide: $(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_2CO + C_2H_6$	None	173.5	---	---	1	428	2420	4.63	11
2	Decomposition of dimethyl ether: $(CH_3)_2O \rightarrow CH_4 + H_2 + CO$	None	312	---	---	1	777	4430	8.47	12
3	Decomposition of acetaldehyde: $CH_3CHO \rightarrow CH_4 + CO$	None	365	---	---	2	791	2520	6.11	13
4	Decomposition of azoisopropane: $C_3H_7NNC_3H_7 \rightarrow N_2 + C_6H_{14}$	None	35.15	---	---	1	543	2250	7.60	14
5	Decomposition of 2, 5-dihydrofuran vapor: $OCH_2CHCHCH_2 \rightarrow OCHCHCHCH + H_2$	None	10.938	---	---	1	669.7	2460	10.5	15
			11.632	---	---	↓	665.0	2360	10.8	↓
			11.552	---	---		654.7	2470	11.2	
			11.130	---	---		636.1	2390	12.3	
			10.975	---	---		628.6	2400	12.7	
6	Reduction of Pu(IV) by Fe(II) in perchloric acid solution: $Pu(IV) + Fe(II) \rightarrow Pu(III) + Fe(III)$	0.5 M $HClO_4$	---	0.001148	0.001167	2	293.4	1190	2.85	15
				.001148	.001166	↓	288.6	1180	3.39	↓
				.001148	.001167		283.4	1150	3.92	
				.001149	.001168		279.4	1120	4.46	
				.001140	.001156		275.7	1100	4.96	
7	Reaction of sodium cyanide with methyl iodide in aqueous solution: $CN^- + CH_3I \rightarrow I^- + CH_3CN$	Water	---	0.063	0.0334	2	319.3	1290	8.54	17
				.063	.0342	↓	304.2	1240	9.89	↓
				.063	.0254		293.7	1160	11.3	
				.055	.0266		284.6	1140	12.5	
8	Reaction of sodium cyanide with tris-(1, 10-phenanthroline)-Fe(II): $2CN^- + Fe(Phen)_3(II) \rightarrow Phen + Fe(Phen)_2(CN)_2$	Water	---	0.105	0.0000313	2	298	1530	8.88	18
				.105	↓	↓	283	1200	11.7	↓
				.239			298	1680	8.95	
				.239			283	1250	11.4	
9	Reaction of potassium ferricyanide with 2-mercaptoethanol in aqueous solution: $2Fe(CN)_6^{-3} + 2ESH \rightarrow 2Fe(CN)_6^{-4} + ESSE + 2H^+$ where ESH is 2-mercaptoethanol and ESSE is bis-β-oxyethyl disulfide	Water	---	0.00110	0.0189	2	273	962	-----	19
				.00119	.0206	2	273	992	-----	19
10	Reaction of cis-2-butene episulfide with triphenylphosphine: $CH_3HCSCHCH_3 + (C_6H_5)_3P \rightarrow CH_3HCCHCH_3 + (C_6H_5)_3PS$	m-xylene	---	0.314	0.314	2	313	1240	12.0	20
		N, N-dimethyl-formamide	---	.308	.308	2	313	1230	11.6	20
		Cyclohexanone	---	.301	.301	2	313	1250	11.9	20
11	Decomposition of trans-dimeric methylnitroso: $(CH_3NO)_2 \rightarrow 2CH_3NO$	Ethanol	---	0.0000361	---	1	338	1380	13.2	21
				.0000361	---	1	333	1270	14.2	21
12	Reaction of bis-p-chlorophenylmercury with mercuric iodide: $Hg(ClC_6H_4)_2 + HgI_2 \rightarrow 2(ClC_6H_4)HgI$	Dioxane	---	0.001	0.001	2	318	1380	7.89	22
				.001	.001	2	308	1360	12.9	22
13	Reaction of bis-p-fluorophenylmercury with mercuric iodide: $Hg(FC_6H_4)_2 + HgI_2 \rightarrow 2(FC_6H_4)HgI$	Dioxane	---	0.001	0.001	2	318	1290	6.59	22
				.001	.001	2	308	1280	7.27	22

[a]Where t_1 is in seconds.



(a) Temperature, 525° K. (b) Temperature, 552° K. (c) Temperature, 583° K.

Figure 1. - Dehydrogenation of isobutane by iodine.

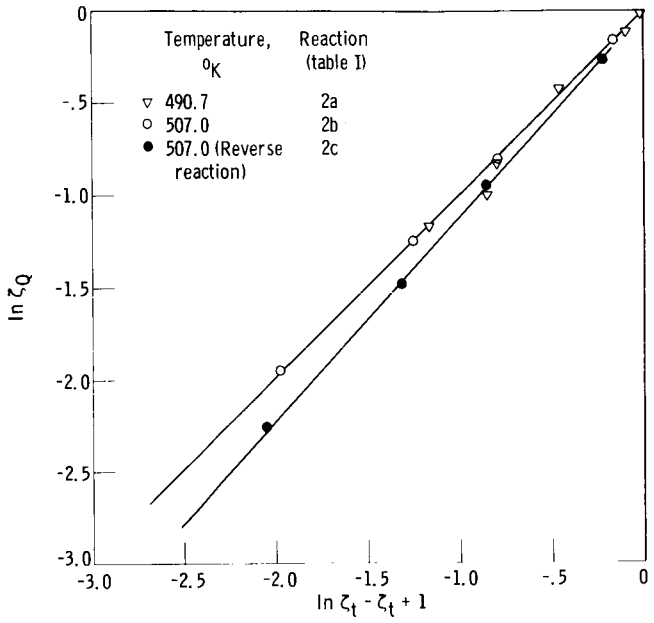
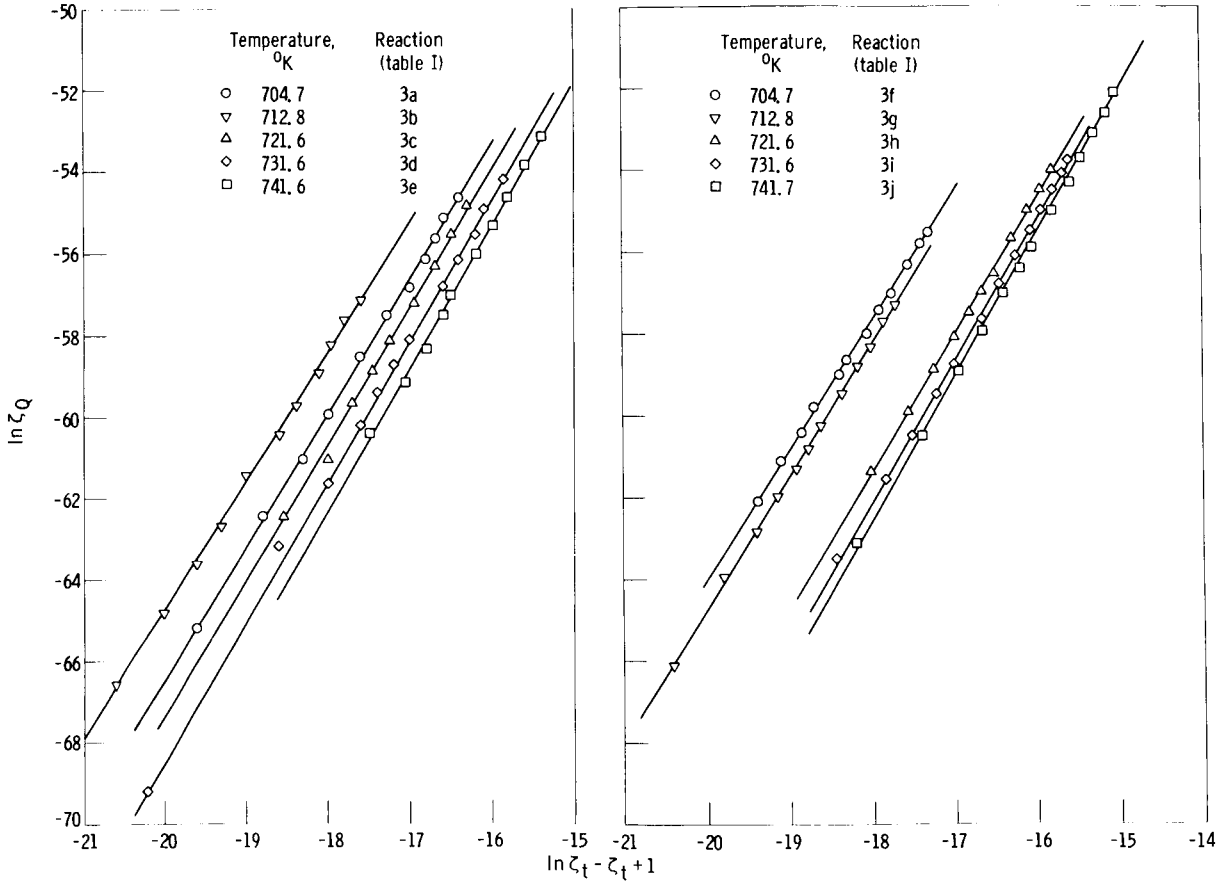


Figure 2. - Conversion of ethylidenecyclopropane to 2-methylmethylene-cyclopropane.

value of t_K is assumed to be very large compared with the experimental period of observation. The constant C_2 can be interpreted in terms of a kinetic parameter t_1, defined as the time at which the activity quotient is 1. Equation (14) can then be expressed as

$$\ln Q = \frac{A_r}{RT} \ln\left(\frac{t}{t_1}\right) \qquad (20)$$

The values of the parameters A_r and t_1 for 13 homogeneous stoichiometric reactions are listed in table II (p. 8).



(a) Helium, 66.7 mole percent; initial total pressure, 28.8 torr. (b) Helium, 83.3 mole percent; initial total pressure, 57.6 torr.

Figure 3. - Decomposition of hydrogen peroxide with helium.

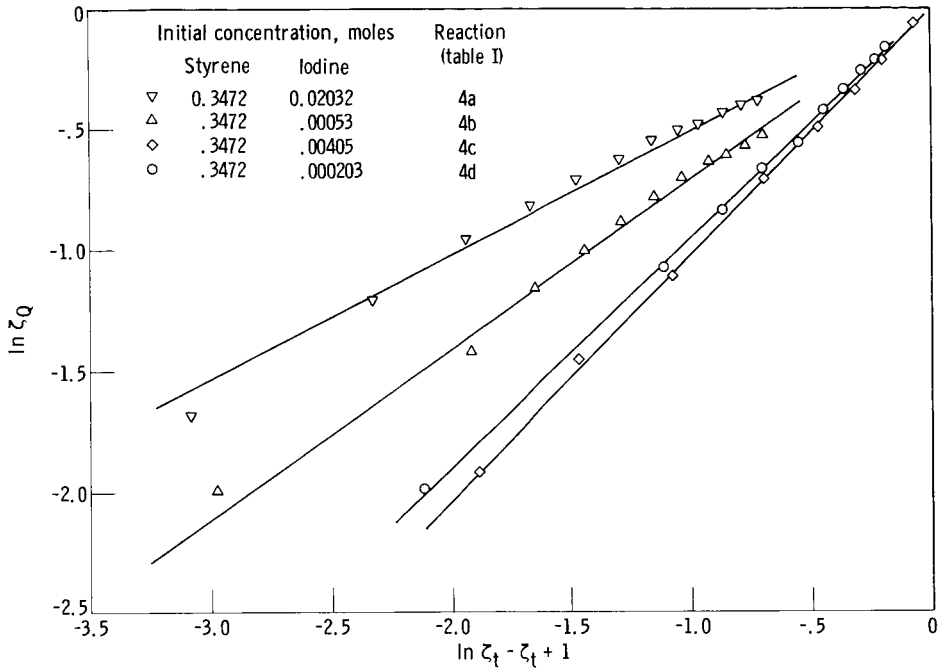


Figure 4. - Reaction of styrene and iodine in carbon tetrachloride at 295° K.

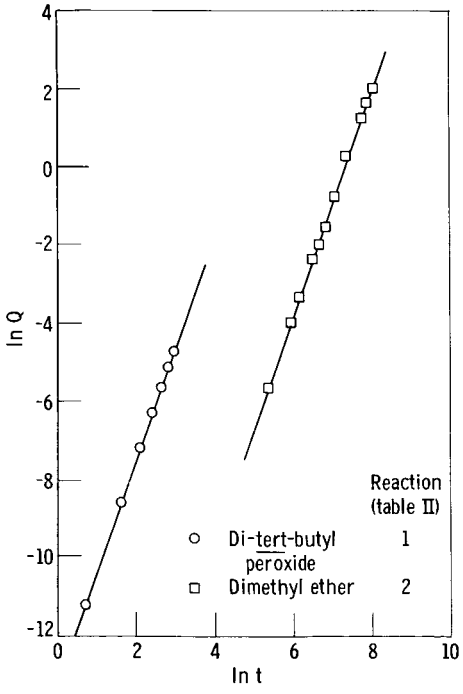


Figure 5. - Decomposition of di-tert-butyl peroxide and dimethyl ether.

GRAPHICAL PRESENTATION OF EMPIRICAL DATA

Figure 1 (p. 9) illustrates the dehydrogenation of isobutane by iodine at three temperatures and at various initial concentrations of the reactants. The correlation between the activity quotient and the elapsed time was good under all the conditions of observation.

Figure 2 illustrates both the forward and the reverse reaction between ethylidenecyclopropane and 2-methylmethylenecyclopropane. The degree of correlation was reasonably good in both directions, despite the few data points available.

The decomposition of hydrogen peroxide vapor in helium is illustrated in figure 3 for five temperatures and two initial helium pressures. A linear correlation is observed at the 10 experimental conditions.

The reaction of styrene and iodine in carbon tetrachloride at four initial concentrations of iodine (fig. 4) did show deviations from linearity at two

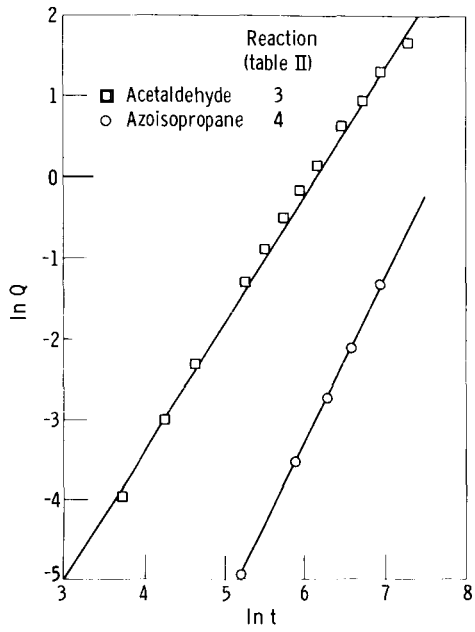


Figure 6. - Decomposition of acetaldehyde and azoisopropane.

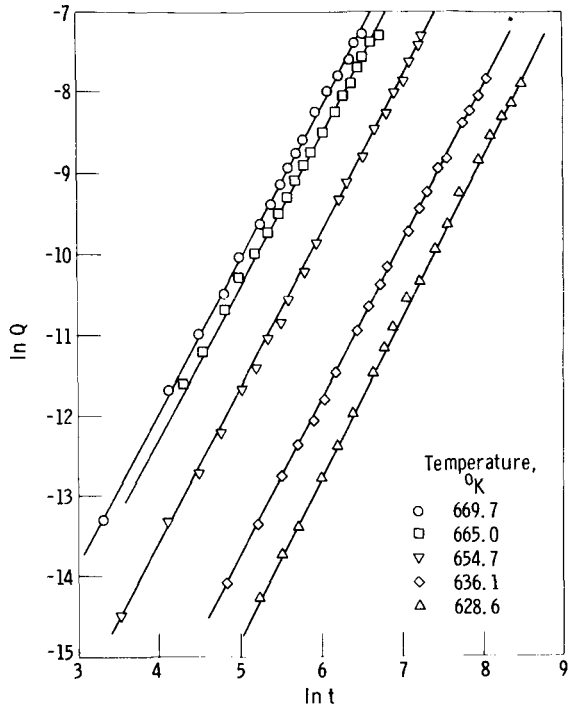


Figure 7. - Decomposition of 2,5-dihydrofuran vapor (table II, reaction 5).

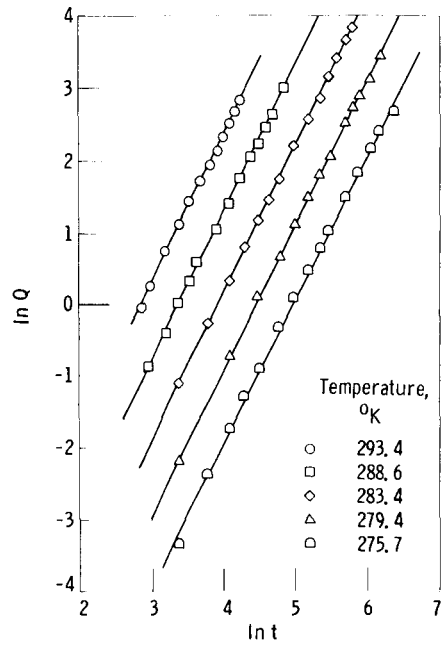


Figure 8. - Reduction of Pu(IV) by Fe(II) in 0.5 M perchloric acid solution (table II, reaction 6).

initial concentrations, but two of the runs did show a good correlation according to equation (19).

Figures 5 to 13 illustrate the correlation between the activity quotient Q and the elapsed time t according to equation (20) for the 13 reactions listed in table II (p. 8). Figures 5 to 7 illustrate gas-phase reactions; the remainder show liquid-phase reactions. The first three liquid-phase reactions occur in aqueous solution. In most cases, the first 60 percent of each reaction was observed, but in no case was less than 20 percent observed.

Figures 5 and 6 illustrate the thermal decomposition of four organic compounds. The correlation between the activity quotient and the elapsed time is reasonably good for these reactions, although some deviations were observed, most easily noticed in the case of the decomposition of acetaldehyde. Similar deviations from linearity were found for other organic decomposition reactions in which small amounts of hydrogen, carbon oxides, or simple hydrocarbons were found

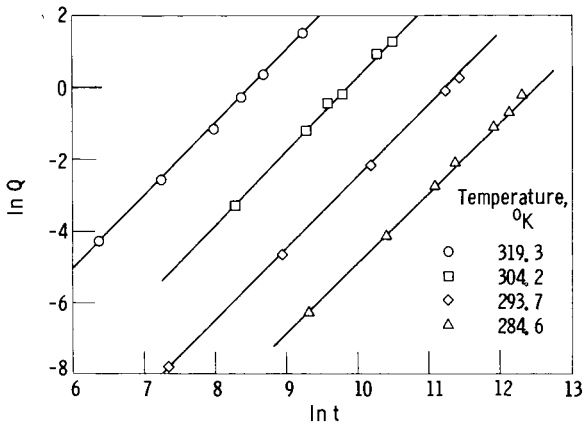


Figure 9. - Reaction of sodium cyanide with methyl iodide in aqueous solution (table II, reaction 7).

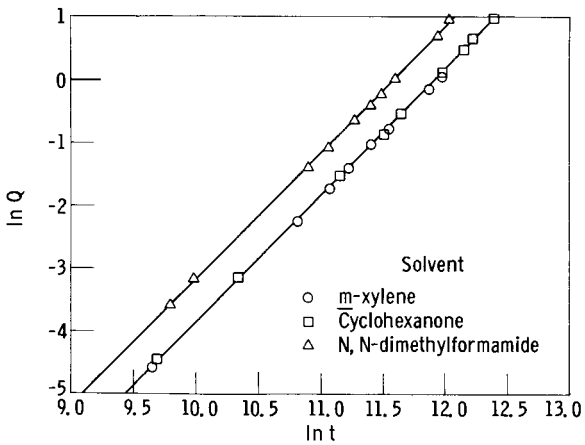


Figure 11. - Reaction of cis-2-butene episulfide with triphenylphosphine (table II, reaction 10).

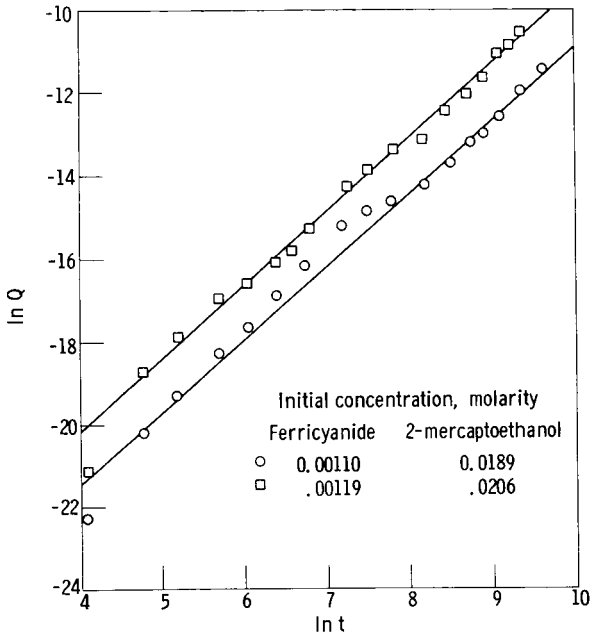


Figure 10. - Reaction of potassium ferricyanide and 2-mercaptoethanol in aqueous solution (table II, reaction 9).

with the primary products, which indicated a nonstoichiometric reaction.

The correlation of the kinetic data for the decomposition of 2, 5-dihydrofuran vapor (fig. 7) was very good at the five temperatures of observation.

Figure 8 illustrates an electron-transfer reaction in perchloric acid solution. The correlation was good at the five temperatures at which this second-order reaction was observed. Other electron-transfer reactions in perchloric acid solutions also show good correlations.

Figure 9 illustrates an ionic reaction in aqueous solution at four temperatures. As in the case of the electron-transfer reactions, a linear correlation was observed.

The reaction between ferricyanide and 2-mercaptoethanol in aqueous solution does not show so good a correlation as do the other reactions in aqueous solution. The data points are somewhat erratic, as shown in figure 10.

The correlation between the activity quotient and the elapsed time is generally good for reactions in nonaqueous solutions. The reaction of cis-2-butene episulfide with

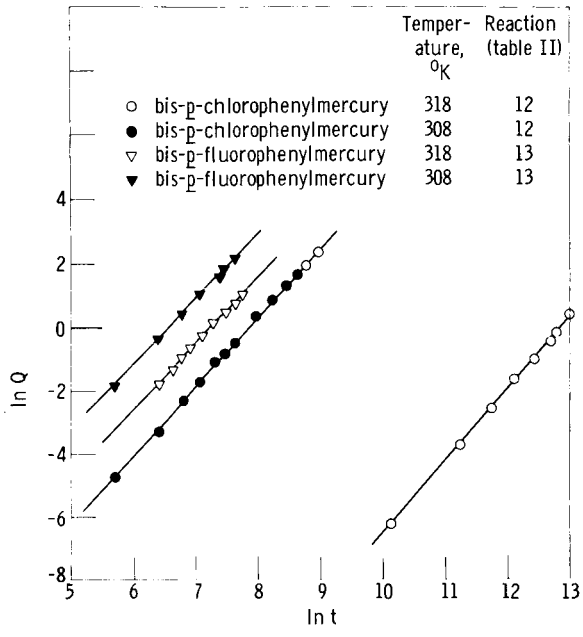


Figure 12. - Reaction of bis-p-chlorophenylmercury and bis-p-fluorophenylmercury with mercuric iodide in dioxane.

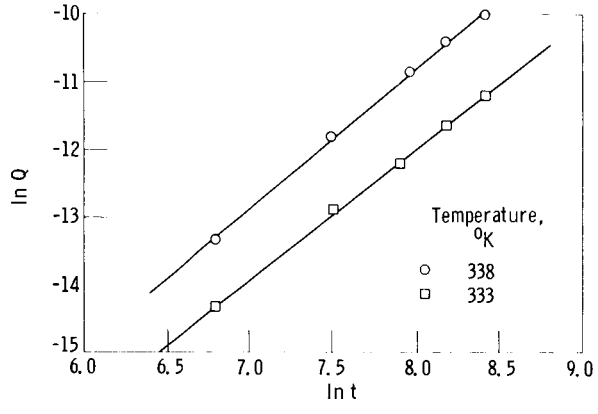


Figure 13. - Decomposition of trans-dimeric methylnitroso in ethanol (table II, reaction 11).

triphenylphosphine in three organic solvents shows a high degree of correlation, as illustrated in figure 11. The reactions illustrated in figures 12 and 13 occur in dioxane and ethanol, respectively, and also show good correlations.

STATISTICAL ANALYSIS

The empirical data supplied by the various investigators were statistically analyzed to determine how well they were correlated by equations (19) and (20). The 3σ confidence limits of the determination coefficient were computed for each reaction. For more than two-thirds of the 113 reactions investigated, the lower confidence limit exceeded 95 percent, which indicated a good correlation. One-half of the reactions investigated had a lower confidence limit greater than 99 percent, which indicated an excellent correlation of the empirical data. This degree of correlation was at least equal to that attained with the appropriate empirical rate equation.

Equilibrium data were not available for the great majority of reactions observed, and it is possible that for some of the reactions that did not correlate well the assumption $t_K >> t$ in equation (14) was not valid. Of the four reactions listed in table I (p. 7), this assumption would have been valid only for the decomposition of hydrogen peroxide.

The 113 reactions investigated were distributed among those reported to be zero, first, second, third, and complex order, as illustrated in table III. The lack of dependency of the correlations on the order of the reactions observed is in accord with the thermodynamic nature of the affinity, for which a mechanistic description is unnecessary.

TABLE III. - DISTRIBUTION OF THE 113 REACTIONS INVESTIGATED AMONG VARIOUS ORDERS

Determination coefficient	Number of reactions correlated for order indicated					Total
	0	1	2	3	Complex	
Good (>95 percent)	1	26	36	8	7	78
Poor (<95 percent)	1	12	16	3	3	35

DISCUSSION

The sole justification for the kinetic approach used herein lies in its ability to describe the kinetic behavior of a large number of chemical reactions without recourse to mechanistic considerations. Such a nonmechanistic description may be possible because the kinetic variables considered, Q and A, are associated with the progress of the entire reacting system and not directly with the change of concentration of a single reacting specie. This view of a chemical reaction as a homogeneous "consumer" of affinity and not as a system of individual reacting species is the most significant departure of this approach from the customary manner of examining chemical reactions.

Whether there exists also a theoretical justification for this approach is beyond the scope of this empirical study.

The concept of t_K as a finite quantity was a necessary outcome of relation (11) to satisfy the kinetic condition at equilibrium that the overall rate of reaction is zero and the thermodynamic condition that the activity quotient is equal to the equilibrium constant. Although it is intuitively thought that the time to attain equilibrium must be infinite, it has been observed that many reactions reach a state indistinguishable from equilibrium in a finite length of time. In ionic reactions, for example, such as the neutralization of a strong acid by a strong base, a state indistinguishable from equilibrium is apparently attained when the reactants meet. A consequence of the concept of t_K as a finite quantity is discussed in the appendix.

The affinity, which can be considered on a thermodynamic basis as an indication of the tendency for reaction, can also be considered on a kinetics basis as an indication of the extent of reaction. At equilibrium, equation (8) reduces to

$$A^O = RT \ln K \tag{21}$$

Substituting this value for the standard affinity back into equation (8) yields

$$A = -RT \ln \zeta_Q \tag{22}$$

Equation (22) is essentially the form used by Prigogine, Outer, and Herbo (ref. 4) to express the affinity in terms of the reacting components. Equation (22) can be combined with equation (19) to yield

$$A = -A_r(\ln \zeta_t - \zeta_t + 1) \tag{23}$$

Thus, for homogeneous stoichiometric reactions, the kinetic behavior of which is adequately described by relation (11), the affinity can be related to the elapsed time by equation (23), for which A_r can be considered the affinity-rate coefficient.

CONCLUDING REMARKS

The linear phenomenological equations, introduced ad hoc into the theories of irreversible thermodynamics as a means of relating forces and flows, have proven to be inadequate in describing the kinetic behavior of actual chemical reactions. Other approaches have been sought.

In this study, the thermodynamic force itself is considered a function of time, with the flow (the rate of production or consumption of an individual reacting specie) disregarded. The decay of the force as a reaction proceeds towards equilibrium is thus the sole kinetic variable considered.

It was necessary to introduce an empirical relation to describe the kinetics of the reactions investigated in terms of the thermodynamic force or affinity. In accordance with the thermodynamic nature of this description, the degree of correlation achieved was independent of the mechanisms of the individual reactions.

For the majority of the reactions investigated, the affinity varied with time according to a single relation.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 30, 1965.

APPENDIX - PREDICTION OF EQUILIBRIUM CONSTANTS

Equation (19) can be represented as

$$\ln Q = \frac{A_r}{RT} (\ln \zeta_t - \zeta_t + 1) + \ln K \qquad (A1)$$

Relating the empirical data according to equation (A1) should result in an intercept equal to the equilibrium constant for the reaction investigated. The value of t_K, however, must be known before such a determination can be made. One method is to use the value of t_K that best correlates the empirical data, that is, to vary the value of this term until the determination coefficient is at a maximum.

The question of whether, in fact, equilibrium constants can be predicted from kinetic data was examined by correlating three of the reactions listed in table I (p. 7) according to equation (A1). The conversion of ethylidenecyclopropane was not tested because too few data points were available. The values of the intercept and the determination coefficient were found for various values of t_K (fig. 14). The value of the determination coefficient reached a sharp maximum at the value of the intercept that closely approximated the experimental value of $\ln K$ for the reactions considered. The points on the abscissa indicate these experimental values.

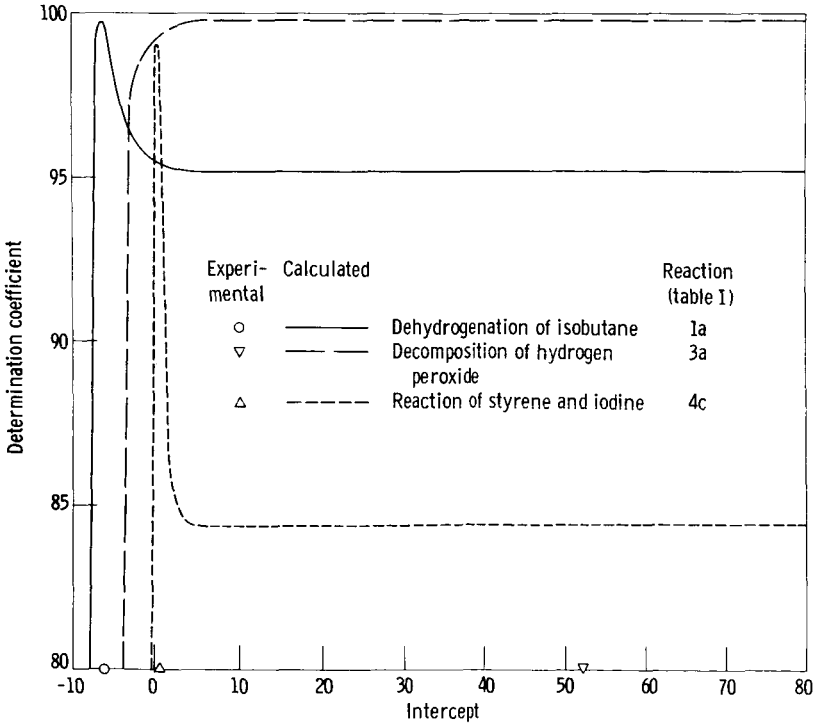


Figure 14. - Variation of intercept of equation (A1) with determination coefficient.

TABLE IV. - COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF EQUILIBRIUM CONSTANTS

Reaction number	Reaction	Equilibrium constant, K		Error, percent
		Calculated	Thermodynamic	
1a	Dehydrogenation of isobutane by iodine: $C_4H_{10} + I_2 - 2HI + C_4H_8$	0.00252	0.00215	17.2
1b		.00187	.00234	20.0
1c		.00634	.00766	17.2
1d		.00666	.00783	14.9
1e		.00651	.00783	16.8
1f		.0195	.0258	24.4
1g		.00798	.0263	69.9
1h		.0214	.0255	16.0
4a	Reaction of styrene with iodine in carbon tetrachloride: $C_6H_5CHCH_2 + I_2 - C_6H_5CHI_2CH_2$	0.764	1.10	30.9
4b		.651	↓	40.9
4c		1.26	↓	14.5
4d		1.27	↓	15.5

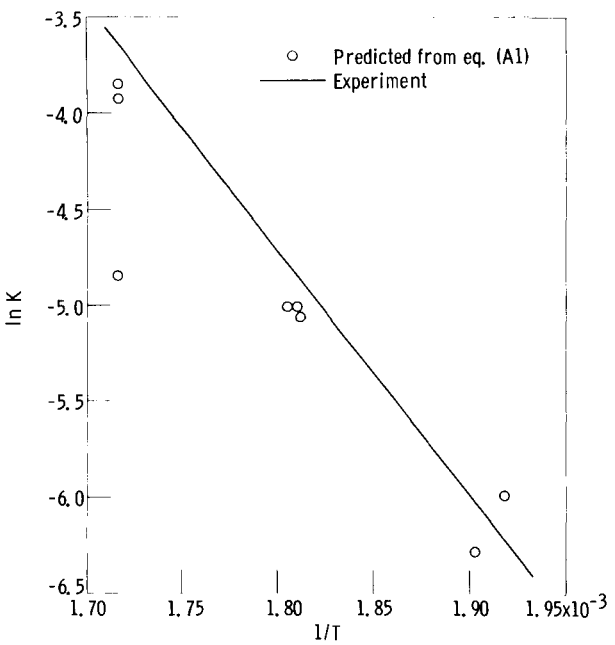


Figure 15. - Comparison of equilibrium constants at various temperatures predicted from equation (A1) with curve determined from direct measurements for dehydrogenation of isobutane (ref. 6).

The agreement between the experimental and the predicted values of the equilibrium constants for the dehydrogenation of isobutane by iodine and for the reaction of styrene with iodine is very good, as shown in table IV. Figure 15 illustrates the values of the equilibrium constants predicted from equation (A1) at various temperatures as compared with the experimental curve. With the exception of one point, the agreement was good.

In the case of hydrogen peroxide, the range of observation of the experimental data is so far removed from the equilibrium state that there is considerable uncertainty in the maximum value of the determination coefficient, as illustrated in figure 14. This uncertainty is manifested in the absence of a discernible peak.

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