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GAS-PHASE ELEMENTARY CHEMICAL REACTIONS

Harold S. Johnston

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GAS-PHASE ELEMENTARY CHEMICAL REACTIONS

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A. Introduction

One should be careful to define what is meant by "elementary reaction." Otherwise, a physicist may deny that this reaction is elementary

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

because of the spread of quantum states of the reactants. Also, a chemist may deny that this is a reaction

$$\underbrace{O(^1D) + Ne}_{\text{relative velocity 1}} \rightarrow \underbrace{O(^3P) + Ne}_{\text{relative velocity 2}} \tag{2}$$

because there is no change of chemical bonding. Each of these is an elementary process, but in a different sense of the word.[1,2]

<u>Elementary Physical Reactions</u>. - An <u>ideal</u> elementary physical reaction is illustrated by[3]

$$\underbrace{O_2\ (^3\Sigma_g^-,\ v = 2,\ J = 13) + Ne}_{\text{relative velocity 1}} \rightarrow \underbrace{O_2(^3\Sigma_g^-,\ v = 1,\ J = 15) + Ne}_{\text{relative velocity 2}} \tag{3}$$

In principle, the relative velocity of reactants could be determined by a rotating-sector with crossed molecular beams; and the precise electronic, vibrational, and rotational states of reactants could be selected and known. Likewise the detector system could be such that relative velocity and detailed internal states of the reactants are determined. Even in this ideal experiment the reactants approach each other with a random spread of impact

parameter, and thus the observed reaction cross section is an average over orbital angular momentum.

Whereas the ideal elementary physical reaction involves knowledge of all quantum states before and after the transition occurs, the general term "elementary physical reaction" is broadened to include any inelastic collision process with a known change of any type of internal quantum number. An example is vibrational energy transfer with averaging over rotational states and over impact parameter

$$\underbrace{O_3(^1A,\ v_1,\ v_2,\ v_3) + Ar}_{\text{relative velocity 1}} \rightarrow \underbrace{O_3(^1A,\ v_1',\ v_2',\ v_3') + Ar}_{\text{relative velocity 2}} \qquad (4)$$

A simple vibrational energy transfer might involve averaging over velocities, impact parameter, and rotational states

$$O_2(^3\Sigma_g^-,\ v = 1) + Ar \rightarrow O_2(^3\Sigma_g^-,\ v = 0) + Ar \qquad (5)$$

Certain interactions of radiation and molecules may be classified as elementary physical processes, such as,

$$O_2(^3\Sigma_g^-) + h\nu \rightarrow O_2(^1\Delta_g) \qquad (6)$$

Both fluorescence and Raman scattering should be included under this term.

Elementary Chemical-Physical Reactions. - An ideal elementary chemical-physical reaction involves a collision process of known relative velocity, with a change in molecular structure, and with all quantum states of reactants and products known,[4] for example

$$\underbrace{O(^3P) + O_3(^1A,\ v_1,\ v_2,\ v_3,\ J,\ K_a,\ K_b)}_{\text{relative velocity 1}}$$

$$\rightarrow \underbrace{O_2(^3\Sigma_g^-,\ v,\ J) + O_2(^1\Delta_g,\ v,\ J)}_{\text{relative velocity 2}} \qquad (7)$$

Rarely, if ever, is the ideal case realized. The term "elementary chemical-physical reaction" is broadened to include any collision process leading directly to a change in molecular structure, for which some quantum state of reactants and products is known. A chemical change in velocity-selected, crossed molecular beams is an example,[5,6,7]

$$K + HBr \rightarrow KBr + H$$

$$Cs + RbCl \rightarrow CsCl + Rb \qquad (8)$$

$$N_2^+ + H_2 \rightarrow N_2H^+ + H$$

A reaction which forms products in a known vibrational state is an elementary chemical-physical process[8,9,10]

$$O(^3P) + NO_2(^2A_1) \rightarrow NO(^2\Pi_{1/2}) + O_2(^3\Sigma_g^-,\ v = 19) \qquad (9)$$

$$2\ O(^3P) + M \rightarrow O_2(^3\Sigma_g^-,\ v = 12) + M$$

$$H + Cl_2 \rightarrow Cl + HCl + \text{infrared emission}$$

Photodissociation reactions[11] may be in this class

$$O_3(^1A) + h\nu(3000A) \rightarrow O_2(^1\Delta_g) + O(^1D) \qquad (10)$$

Chemical activation[12] leads to products with a precisely-known, very high internal energy

$$H + C_2H_4 \rightarrow C_2H_5^* \tag{11}$$

Photodissociation with monochromatic radiation may[13] lead to products with known translation energy

$$HI + h\nu \rightarrow \underbrace{H + I}_{\text{relative velocity}} \tag{12}$$

B. Elementary Chemical Reactions

Examples. - Although it is fairly simple to define the term "elementary chemical reaction", a number of examples will be given before a formal definition is presented. Bimolecular hydrogen-atom-transfer reactions, such as,

$$Cl + H_2 \rightarrow HCl + H \tag{13}$$

$$CH_3 + CD_4 \rightarrow CH_3D + CD_3$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4$$

$$CH_3O + HNO \rightarrow CH_3OH + NO$$

occur with a simple second-order rate law, $\underline{k}[A][B]$. The second-order rate constant $\underline{k}$ is a simple function of temperature, the Arrhenius equation

$$\underline{k} = \underline{A} \exp(-\underline{E}/\underline{R}\,\underline{T}) \tag{14}$$

The rate constants are smoothly related to molecular properties of reactants, which can be expressed in several simple ways.[14]

The oxides of nitrogen are particularly versatile in illustrating principles of chemistry. Bimolecular reactions of oxides of nitrogen have been extensively studied, for example,

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{15}$$

$$NO + NO_3 \rightarrow NO_2 + NO_2$$

$$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$$

$$NO_3 + NO_3 \rightarrow NO_2 + O_2 + NO_2$$

These reactions follow second-order rate laws, and the rate constant is a function of temperature. The values of the rate constants are not readily expressed in terms of simple molecular properties, but the Arrhenius A-factors are easily rationalized in terms of thermodynamic properties of the reactants and postulated structures of intermediate collision complexes.[15]

One set of similar bimolecular reactions seemed to give rate constants that made no sense at all in terms of molecular properties of the reactants and products. The set was presumed to be elementary, bimolecular, four-atom, four-center reactions

	E(kcal)	A(cc/sec)	ΔH°(kcal)	
$ClO + ClO \rightarrow Cl_2 + O_2$	~ 0	10^{-13}	-50	(16)
$NO + NO \rightarrow N_2 + O_2$	64	4×10^{-12}	-43	
$HI + HI \rightarrow H_2 + I_2$	44	6×10^{-11}	+ 3	

Recent re-investigations have shown that none of these reactions is "four center" or elementary as written. The actual elementary reactions are[16,17,18]

	E	ΔH°	
$ClO + ClO \rightarrow Cl + ClOO$	~ 0	~ 0	(17)
$NO + NO \rightarrow N_2O + O$	64	+36	
$HI + HI \rightarrow I + H_2 + I$	44	+40	

This relation between activation energy and enthalpy of reaction is much more reasonable than that of Equation (16). Subsequent reactions of Cl, O, and I atoms lead to the molecular products shown in Equation (16).

Elementary unimolecular chemical reactions at the "high pressure limit", such as,[19,20a]

$$CH_3NC \rightarrow CH_3CN \qquad P > 10 \text{ atm.} \qquad (18)$$

$$N_2O_5 \rightarrow NO_2 + NO_3 \qquad P > 10 \text{ atm.}$$

follow a first-order rate law $-d[A]/dt = \underline{k}[A]$ and the first-order rate constant depends only on temperature

$$k = k(T) \tag{19}$$

On the other hand, these same reactions at the "low pressure limit" follow the first-order rate law throughout a given experiment, but the first-order rate constant itself depends on reactant concentration and on the pressure of added foreign gas

$$\underline{k} = \underline{k}_A[A] + \underline{k}_M[M] = \underline{k}_A([A] + \alpha_M[M]) \tag{20}$$

where $\alpha_M = \underline{k}_M/\underline{k}_A$. The "relative efficiency" of foreign gas α_M varies with identity of the gas M; for the decomposition[20b] of N_2O_5 with the gases He, N_2, CO_2, CCl_4 the values of α_M are respectively 0.12, 0.23, 0.40, and 0.55.

The decomposition of diatomic molecules[21] occurs with a rate law like that of a polyatomic molecule at its low pressure limit. The rate is second order, first order in reactant and first order in total gas M. The magnitude of the second order rate constant depends on the identity of gas M as well as the temperature T. The recombination of atoms[22] follows a third order rate law, and the rate constant depends on the identity of the foreign gas and on the temperature.

An elementary reaction ($A \rightarrow$ products) has a first-order rate constant $\underline{k}$ that depends only on temperature at high pressures but depends on temperature, concentration of gases [M], and identity

of added gases M at low pressure, Equation (20). At intermediate pressures the first-order rate constant shows a continuous trend between its high-pressure value and its low-pressure value. Throughout this range of pressures, the observed rate constant depends (in a reproducible manner) on three macroscopic variables:

1. Temperature
2. Identity of gases, M
3. Concentration of gases, [M].

This dependency may be abbreviated as

$$\underline{k} = \underline{k}(\underline{T},\ M,\ [M]) \tag{21}$$

The explanation of this effect has a long and interesting history, from Lindemann[23] in 1922 to the latest volume of the Journal of Chemical Physics.[24] The simplest statement of the situation is that molecules are activated in vibrational modes by collision a, deactivated by collisions b, and the activated molecule may spontaneously decompose by a unimolecular process c

$$\begin{aligned} A + M &\xrightarrow{\underline{a}_M} A^* + M \\ A^* + M &\xrightarrow{\underline{b}_M} A + M \\ A^* &\xrightarrow{\underline{c}} \text{products} \end{aligned} \tag{22}$$

The steady-state treatment of the intermediate activated molecule gives its distribution function as

$$\frac{[A^*]}{[A]} = \frac{\underline{a}_M[M]}{\underline{b}_M[M] + \underline{c}} \tag{23}$$

The rate of reaction is simply

$$-\frac{d[A]}{dt} = \underline{c}[A^*] = \frac{\underline{a}_M\underline{c}[A][M]}{\underline{b}_M[M] + \underline{c}} \tag{24}$$

The empirical first-order rate constant thus may be expressed as

$$\underline{k} = \frac{\underline{a}_M\underline{c}[M]}{\underline{b}_M[M] + \underline{c}} \tag{25}$$

where the explicit form of dependence on identity of M (in terms of $\underline{a}_M$ and $\underline{b}_M$) and concentration of M is given (realistic forms of this theory,[24] of course, give the rate in terms of individual vibrational quantum states or density of states at various degrees of excitation energy). The competition in rate between the energy-transfer step $\underline{b}$ and the molecular decomposition $\underline{c}$ leads to a highly non-equilibrium distribution, Equation (23), since the equilibrium distribution of A^* is $\underline{a}/\underline{b}$.

Elementary Chemical Reactions in Terms of Elementary Molecular Processes. - If expressed in terms of individual vibrational and rotational states of the excited molecule,[25] the decomposition of excited molecules

$$[N_2O_5]_i \rightarrow \underbrace{[NO_2]_m + [NO_3]_n}_{\text{relative velocity, } g} \tag{26}$$

is an elementary chemical-physical reaction. The activation and deactivation of the molecule to a specific excited state $\underline{i}$ are examples of elementary physical reactions. The actual distribution of reactant molecules is determined by competition between energy-transfer rates and chemical-physical reaction rates. This actual distribution over excited states is never literally the equilibrium distribution so long as a net reaction is taking place. During reaction the distribution of reactants over internal excited states is

$$\underline{P}_i = \frac{[A_i]}{[A]} = \frac{\underline{a}_i[M]}{\underline{b}_i[M] + \underline{c}_i} \tag{27}$$

At equilibrium this distribution function is

$$\left(\underline{P}_i\right)_{eq.} = \left(\frac{[A_i]}{[A]}\right)_{eq.} = \frac{\underline{a}_i}{\underline{b}_i} \tag{28}$$

Although $\underline{P}_i$ and $(\underline{P}_i)_{eq.}$ are never identically the same, at a sufficiently high pressure the difference in the two becomes negligible. Whereas the actual distribution $\underline{P}_i$ depends on temperature, identity of M, and concentration of M, in the high pressure region $\underline{P}_i$ is excellently approximated by $(\underline{P}_i)_{eq.}$; and then $\underline{P}_i$ depends only on the temperature. Therefore, the rate constant of a unimolecular reaction in the high pressure region varies only with temperature, Equation (19).

The interpretation of elementary chemical rate constants in terms of the component elementary physical and chemical-physical processes may also be set up for bimolecular reactions, for example.

$$NO_2 + CO \rightarrow NO + CO_2 \tag{29}$$

The rate of reaction and the rate constant are defined by

$$\frac{-d[NO_2]}{dt} = \underline{k}[NO_2][CO] \tag{30}$$

The observed rate is a sum over the actual distribution of reactants for elementary molecular processes

$$\underbrace{NO_2(\underline{i}) + CO(\underline{j})}_{\underline{g} = \underline{l}} \xrightarrow{\underline{k}_{i\ j\ l\ m\ n\ p}} \underbrace{NO(\underline{m}) + CO_2(\underline{n})}_{\underline{g} = \underline{p}}$$

Here the symbol $\underline{i}$ stands for the complete internal state, electronic, vibrational, and rotational, of NO_2; and similarly $\underline{j}$, $\underline{m}$, and $\underline{n}$ specify the internal states of the other species. Relative velocity is expressed by the symbol $\underline{g}$. The microscopic rate constant $k_{i\ j\ l\ m\ n\ p}$ is already an average over impact parameters. Formally, the macroscopic rate is a six-fold summation

$$\frac{-d[NO_2]}{dt} = \sum_i \sum_j \sum_l \sum_m \sum_n \sum_p k_{i\ j\ l\ m\ n\ p}([NO_2]_i[CO]_j)_l \tag{32}$$

For each state $\underline{i\ j\ l}$ of the reactants, the sum over all possible states of products leads to the simplification

$$\sum_m \sum_n \sum_p k_{i\ j\ l\ m\ n\ p} = k_{i\ j\ l} \tag{33}$$

For each pair of internal states $\underline{i\ j}$ and for each relative velocity $\underline{l}$, the rate may be expressed in terms of relative velocity $\underline{g}$, reaction cross section $\sigma_{ij}(g)$, and the actual distribution of relative velocities:

$$\frac{-d[NO_2]}{dt} = \sum_i \sum_j \int \sigma_{\underline{ij}}(\underline{g})\ \underline{g}\underline{P}(\underline{g})d\underline{g} \quad [NO_2]_{\underline{i}}[CO]_{\underline{j}} \tag{34}$$

The fraction of molecules of nitrogen dioxide in the state $\underline{i}$ is defined as

$$\underline{P_i} = [NO_2]_{\underline{i}}/[NO_2] \tag{35}$$

and similarly for carbon monoxide

$$\underline{P_j} = [CO]_j/[CO] \tag{36}$$

The macroscopic rate is thus

$$\frac{-d[NO_2]}{dt} = [NO_2][CO]\sum_i \sum_j \int P_i P_j\ \sigma_{ij}(g)\ g\ P(g)dg \tag{37}$$

where the microscopic concentrations, $[NO_2]_{\underline{i}}$ and $[CO]_{\underline{j}}$, are replaced by the macroscopic concentrations, $[NO_2]$ and $[CO]$, according to Equations (35) and (36). The macroscopic rate constant of the elementary chemical reaction is thus expressed as an average over microscopic reaction cross sections $\sigma_{ij}(g)$ and the actual distribution of reactants over translational states $\underline{P}(\underline{g})d\underline{g}$ and internal states, $\underline{P_i}$ and $\underline{P_j}$,

$$\underline{k} = \sum_i \sum_j \int \underline{P}_{\underline{i}} \underline{P}_{\underline{j}} \, \sigma_{\underline{ij}}(\underline{g}) \; \underline{g}\underline{P}(\underline{g}) d\underline{g} \tag{38}$$

Studies of ideal elementary chemical-physical reactions in crossed molecular beams would give the microscopic, molecular reaction cross sections σ. Studies of energy-transfer rates in elementary physical reactions establish the conditions under which the distribution functions, $\underline{P}(\underline{g})$, $\underline{P}_{\underline{i}}$, $\underline{P}_{\underline{j}}$, have essentially an equilibrium distribution function. If the equilibrium distribution is not maintained, a comparison of molecular reaction rates and energy transfer rates permits calculation of the actual steady-state distribution that obtains during the reaction.

Definition. - The definition of an elementary chemical reaction readily follows from the examples given above. An elementary chemical reaction is a given elementary chemical-physical process averaged over a steady distribution of reactants where this distribution can be reproduced by fixing a small number of macroscopic variables, such as, temperature, identity of foreign gas, and pressure of foreign gas. To review the examples cited above, the distribution over states may be adequately reproduced by control of temperature alone for unimolecular reactions at high pressures and for bimolecular reactions

$$A \rightarrow B \text{ or } A \rightarrow B + C, \text{ high pressure} \tag{39}$$

$$A + B \rightarrow C + D$$

In these cases the rate constant depends only on temperature

$$\underline{k} = \underline{k}(T) \tag{40}$$

The third-order rate constant for atom recombination and the second order constant for dissociation of a diatomic molecule

$$\begin{aligned} A + A + M &\rightarrow A_2 + M \\ M + A_2 &\rightarrow M + A + A \end{aligned} \tag{41}$$

depend on both temperature and identity of M

$$\underline{k} = \underline{k}(\underline{T}, M) \tag{42}$$

The first-order rate constant for a general unimolecular reaction and the second-order rate constant for a bimolecular association of polyatomic radicals

$$\begin{aligned} A &\rightarrow B + C, \text{ low pressure} \\ B + C &\rightarrow A, \text{ low pressure} \end{aligned} \tag{43}$$

depend on three macroscopic variables

$$\underline{k} = \underline{k}(\underline{T}, M, [M]) \tag{44}$$

Under extreme conditions of high temperature, short time, non-uniform pressure, high turbulence, etc., the actual distribution of reactants over quantum states may be irreproducible in terms of controllable macroscopic variables. In these cases the concept of elementary chemical reactions breaks down, and the situation must be treated in detail for each special case.

C. Chemical Reactions

An overall reaction as encountered by a chemist is only rarely an elementary chemical reaction[26] (some examples are given by Equations 1, 18, and 29). The usual situation is that a chemical reaction involves reactive intermediates, and the overall process involves two or more elementary chemical reactions. The decomposition of ozone has been extensively studied,[27] and it illustrates the general situation. The overall reaction is

$$2\ O_3 = 3\ O_2 \tag{45}$$

This chemical change ~~reaction~~ is brought about by three elementary chemical reactions

$$\begin{aligned} O_3 + M &\xrightarrow{\underline{k}_1} O_2 + O + M \\ O_2 + O + M &\xrightarrow{\underline{k}_2} O_3 + M \\ O_3 + O &\xrightarrow{\underline{k}_3} 2\ O_2 \end{aligned} \tag{46}$$

The steady-state concentration of the active intermediate, oxygen atoms, is

$$[O] = \frac{\underline{k}_1[O_3][M]}{\underline{k}_2[O_2][M] + \underline{k}_3[O_3]} \tag{47}$$

and the rate expression for the overall reaction is

$$-\frac{d[O_3]}{dt} = \frac{2\ \underline{k}_1\underline{k}_3[O_3]^2[M]}{\underline{k}_2[O_2][M] + \underline{k}_3[O_3]} \tag{48}$$

The rate of the chemical reaction is a complex function of the rates of the component elementary chemical reactions.

A particularly instructive example of the role of elementary chemical processes in predicting overall chemical reactions is given by a set of reactions involving the oxides of nitrogen.[28] The following chemical reactions have been studied very extensively:

$$\underset{\sim}{1}.\quad 2\ N_2O_5 = 4\ NO_2 + O_2 \tag{49}$$

$$\underset{\sim}{2}.\quad NO + N_2O_5 = 3\ NO_2$$

$$\underset{\sim}{3}.\quad 2\ NO_2 + O_3 = N_2O_5 + O_2$$

$$\underset{\sim}{4}.\quad 2\ O_3 + N_2O_5 = 3\ O_2 + N_2O_5$$

The observed rate of reaction $\underset{\sim}{1}$ is first order in N_2O_5 over a wide range of temperature and pressure. However, at extremely low pressures a very strange "fall-off" with pressure is observed. At very high temperatures in a shock tube, the highly reactive radical NO_3 is observed spectroscopically to be an intermediate. The observed rate of reaction $\underset{\sim}{2}$ is the complex expression

$$\frac{-d[N_2O_5]}{dt} = \underline{k}_2[N_2O_5]\ \frac{[NO]}{[NO] + \alpha[NO_2]} \tag{50}$$

At high ratios of NO_2 to NO, the constant α can be found. Under most conditions $\alpha[NO_2] \ll [NO]$, and the observed rate gives the constant $\underline{k}_2$. Reaction $\underset{\sim}{3}$ is simply second order

$$-\frac{d[O_3]}{dt} = \underline{k}_3[NO_2][O_3] \tag{51}$$

Reaction 4 has been studied over an extremely wide range of both reactant ozone and catalyst dinitrogen pentoxide. The empirical rate expression is precisely given by the following, unusual rate law

$$\frac{-d[O_3]}{dt} = \underline{k}_4[O_3]^{2/3}[N_2O_5]^{2/3} \tag{52}$$

The first three of these overall chemical reactions can be quantitatively explained in terms of six elementary chemical reactions

$$\begin{aligned}
&N_2O_5 \xrightarrow{\underline{A}(M)} NO_2 + NO_3 \\
&NO_2 + NO_3 \xrightarrow{\underline{B}(M)} N_2O_5 \\
&NO_2 + NO_3 \xrightarrow{\underline{e}} NO + O_2 + NO_2 \\
&NO + NO_3 \xrightarrow{\underline{f}} NO_2 + NO_2 \\
&NO_3 + NO_3 \xrightarrow{\underline{g}} NO_2 + O_2 + NO_2 \\
&NO_2 + O_3 \xrightarrow{\underline{h}} NO_3 + O_2
\end{aligned} \tag{53}$$

The elementary steps in reaction 1 are A, B, e, f with NO_3 and NO as intermediates present in very low, steady-state concentrations. In reaction 2 the presence of high concentrations of NO as a reactant makes the rate of step e negligible in comparison to step f. Thus the mechanism is A, B, f with NO_3 as steady-state intermediate. Reaction 3 occurs by way of two elementary chemical reactions, h and B, with NO_3 as steady-state intermediate; all other reactions are negligible when both NO_2 and O_3 are present in

macroscopic amounts. From studies of these three chemical reactions under a wide variety of conditions, all six elementary rate constants have been evaluated, A, B, e, f, g, and h.

Reaction 4 involves ozone as reactant and di-nitrogen pentoxide as catalyst. Under these conditions the concentration of nitrogen dioxide is suppressed to a very low value. Both NO_2 and NO_3 are active intermediates, present in low steady-state concentrations. Under these conditions one can use the values of the rate constants A, B, e, f, g, and h to discover that reactions e and f are negligible in this system. Thus the mechanism is found to be the four steps A, B, g, and h. The straightforward application of the steady-state method to NO_2 and NO_3 in this mechanism gives exactly the following rate expression

$$\frac{-d[O_3]}{dt} = \left(\frac{Ah}{B}\right)^{2/3} (2g)^{1/3} [O_3]^{2/3} [N_2O_5]^{2/3} \qquad (54)$$

Thus the mechanism predicts the strange four-thirds order rate expression. If the values of the rate constants, A, B, g, and h, as determined from studies of reactions 1, 2, and 3 are inserted into the theoretical rate expression (54), the predicted rate constant at 300°K is 0.052 in units of moles/cc, sec. The observed value from studies of reaction 4 itself is 0.054 in the same units. The activation energy of reaction 4 based on activation energies observed in the systems 1, 2, and 3 is 20.7 ± 1 kcal/mole. The value observed in a direct study of reaction 4 is also 20.7 ± 1 kcal/mole.

This example illustrates how rate constants of elementary reactions can be transferred from one environment to another to predict the rate of another chemical reaction. In fact, this transfer of elementary rate constants to new situations provides the most powerful prediction that chemical kinetics can make.

The science of gas-phase chemical kinetics has some interesting parallels with the science of chemical thermodynamics. In chemical thermodynamics the fundamental entity is the pure chemical substance, elementary, molecular, or crystalline. It is useful to tabulate in handbooks the thermochemical properties of pure chemical substances. For any chemical reaction, these properties of individual reactants and products can be combined to predict the thermochemical changes that the reaction will bring about. (In chemical thermodynamics it is not useful, in general, to tabulate the thermochemical properties of an impure, unanalyzed substance.) In chemical kinetics, the fundamental entity is the elementary chemical reaction. It is useful to tabulate in handbooks the kinetic properties of elementary chemical reactions, and the National Bureau of Standards of the United States now has an active program underway of preparing such handbooks.[29] For any complex chemical system, the properties of the individual elementary chemical reactions can be combined to predict the kinetic properties of the system as a whole (in chemical kinetics it is not useful, in general, to tabulate the kinetic properties of a complex reaction, where the mechanism is not analyzed in terms of elementary steps). In chemical thermodynamics, the thermochemical

properties are usually listed in terms of the standard state of the pure substance, but in an actual system of chemical interest one must consider actual concentrations or relative amounts of different components. Similarly in kinetics, the handbooks list rate constants for elementary reactions, but the rates depend on rate constants and reactant concentrations.

D. Central Role of Elementary Chemical Reactions

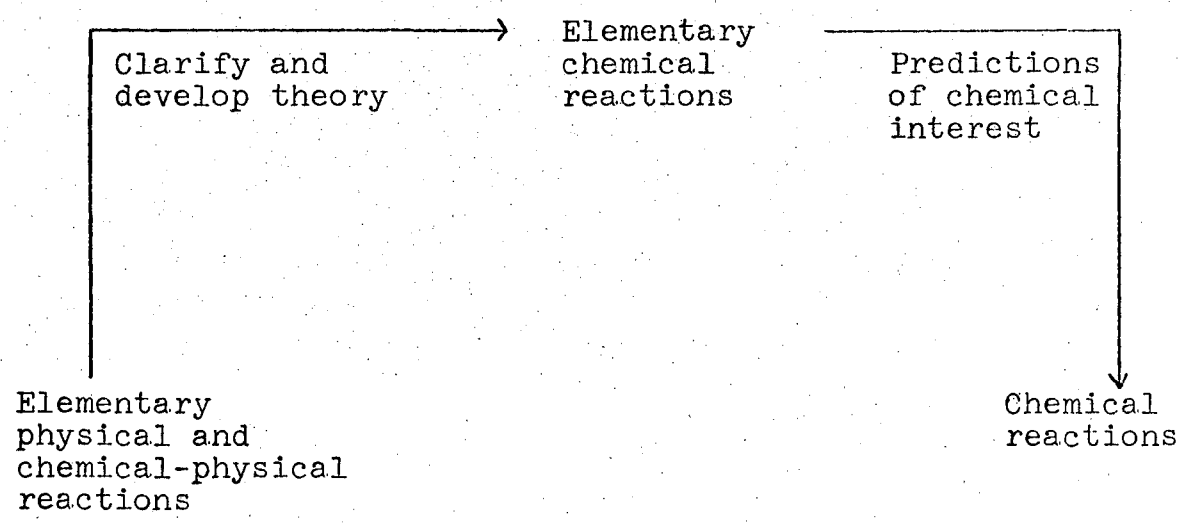
Elementary physical or chemical-physical processes involve an enormous number of sets of quantum states. Molecular beam kineticists and others who work in these fields undoubtedly have little interest in accumulating vast tables of data as ends in themselves. These studies are primarily focussed on the principles involved, not the substances studied. To some extent, the study of molecular beams is a field in itself. To a considerable extent, molecular beam and related studies are devoted to establishing the detailed molecular basis for theories of elementary chemical reactions.

Standard theories of elementary chemical reactions have been forced to make extensive assumptions about the microscopic molecular rate constants and the distribution function over molecular quantum states. The Rice-Ramsperger-Kassel theory[24b] made the (plausible) assumption that the relative molecular rate constant of an excited molecule varied with degree of excitation according to a particular combinatorial formula. Activated complex

theory[30] made the (plausible) assumption that somewhere between reactants and products the collision complex can be expressed in terms of a set of coordinates such that the advancement of the reaction can all be expressed in one coordinate, and the other coordinates are orthogonal to this "reaction coordinate." Simple collision theory assumed that the reaction cross section varies with energy in a particular[31] (plausible) way. In terms of Equation 38, the standard theories have been forced to assume distribution functions, $\underline{P}_{\underline{i}}$, $\underline{P}_{\underline{j}}$, $\underline{P}(\underline{g})d\underline{g}$, and molecular reaction cross sections, $\sigma_{\underline{ij}}(g)$, and to sum over all such variables to get a number to compare with experiment.

The modern kineticist using crossed molecular beams has as one of his goals the direct evaluation of enough molecular reaction cross sections (compare $\sigma_{\underline{ij}}(g)$ in Equation 38) to establish the law of the variation of reaction cross section with molecular states. The various studies of elementary physical reactions can lead to a quantitative understanding of when the assumption of an equilibrium distribution over states is a good approximation and when it is a poor approximation. When the equilibrium approximation is poor, these studies can lead to the actual distribution function, the $\underline{P}$'s of Equation 38. Thus it is to be anticipated that a major product of studies of elementary physical and elementary chemical-physical processes will be a firmer logical base for and improved quantitative predictions from the theories of elementary chemical reactions.

As mentioned above, the field of elementary chemical reactions has now become so mature that it is worthwhile to produce handbooks of data on the rate constants of elementary reactions in terms of the appropriate macroscopic variables, $k(T)$, $k(T, M)$, or $k(T, M, [M])$. These rate constants are uncoupled elements that can be freely transferred from one chemical system to another. Complex rate phenomena can be understood in terms of the elementary steps, and new rate phenomena can be predicted from sets of elementary reactions. In this way tables of elementary rate constants and the theory of elementary chemical reactions can make an important contribution to other areas of chemistry, including chemical problems of the most practical sort. Thus elementary chemical reactions are central to the entire field of kinetics. This relationship is indicated by the diagram



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