

THE PREDICTION OF THERMOCHEMICAL AND KINETIC DATA FOR GAS PHASE REACTIONS.  
CURRENT STATUS.

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**Abstract** - In the past two decades there has been a remarkable growth in reliable experimental data on the Arrhenius parameters for elementary reactions. This includes reactions between neutrals (radicals, atoms, molecules) as well as unimolecular reactions involving these species. In the past decade a parallel and almost equally extensive body of data have begun to accumulate on ion-molecule reactions. The Transition State Theory of Chemical Reactions permits us to organize this experimental data into a relatively simple structure from which we can elucidate a number of simple generalizations which then permit us to make reasonably accurate estimates of the Arrhenius parameters for the rate constants of other, not yet measured elementary processes.

Our ability to use this predictive ability to develop multi-step mechanisms for complex chemical systems rests on a further experimental and empirical base of thermochemical data. Empirical additivity laws can be used to estimate entropies, heat capacities and heats of formation for radicals and large molecules with reasonable precision. Extension of these laws to charged species is examined. Some elementary step reactions in plasmas are compared with their analogues in chain reaction systems.

INTRODUCTION

In the last 20 years our ability to predict thermochemical data and rate parameters has undergone an impressive development. For many classes of molecules and free radicals we can predict these properties with an accuracy equivalent to that of the current experimental, state-of-the-art accuracy. Appearances are that we shall soon be in a position to do that for ions and solvated ions.

To predict the equilibrium constant,  $K_T$  for balanced stoichiometric, chemical reaction we need to know the Gibbs Free Energy change in the reaction,  $\Delta G_T^\circ$ :



$$\Delta G_T^\circ = -RT \ln K_T \quad (2)$$

$$= \Delta H_T^\circ - T\Delta S_T^\circ \quad (3)$$

As indicated in equations 2 and 3,  $\Delta G_T^\circ$  is in turn determined by the enthalpy  $\Delta H_T^\circ$ , and entropy changes  $\Delta S_T^\circ$  in the reaction. It is convenient to reference these latter to some standard temperature (25°C) and pressure (1 atm) and make what usually turns out to be small and generally self-compensating corrections to them in terms of  $\Delta C_{pT}^\circ$ , the heat capacity change in the reaction (1):

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \int_{298}^T (\Delta C_p^\circ) dT \quad (4)$$

$$\Delta S_T^\circ = \Delta S_{298}^\circ + \int_{298}^T (\Delta C_p^\circ) dT/T \quad (5)$$

To make facile use of these relations one is required to have tables of values of  $\Delta H_{f298}^\circ$ ;  $\Delta S_{298}^\circ$  and the molar heat capacity  $C_{pT}^\circ$  of every molecule, radical or ion in equation 1. This

is in general an impossible requirement and so one has resorted to empirical or theoretical methods of predicting these quantities. For small molecules with not more than 2 polyvalent atoms the methods of statistical mechanics have provided sufficient accuracy to predict entropies and heat capacities. To do this one estimates interatomic distances, bond angles and barriers to internal rotation from tables of these quantities. For larger molecules, additivity laws of various sophistication are available for deducing  $S_{298}^{\circ}$  and  $C_{pT}^{\circ}$  from appropriate tables. Entries in these latter relate to structural features such as bonds or groups (Ref.1).

The most elusive property to obtain with accuracy has been  $\Delta H_{298}^{\circ}$ , the standard, molar heat of formation. Where accurate experimental data for key molecules is available, the same additivity laws can be employed to deduce  $\Delta H_{f298}^{\circ}$  for related molecules, radicals or ions in homologous series. This is the case for hydrocarbons, and organic molecules containing oxygen, halogens, nitrogen and sulfur atoms. For other atoms in the periodic table only fragmentary data is available. Even for the first group however there are exceptions (Ref.2). For the best known classes of molecules and free radicals  $\Delta H_{f298}^{\circ}$  is known to  $\pm 0.5$  kcal/mole and  $S_{298}^{\circ}$  and  $C_{pT}^{\circ}$  are known to  $\pm 0.5$  cal/mole- $^{\circ}$ K (e.u.). For the others, the uncertainties are about double this. Table 1 gives the uncertainties in  $K_{eq}$  which arise from these inaccuracies. It shows also the sensitivity of  $S_{298}^{\circ}$  and  $C_p^{\circ}$  to structural features.

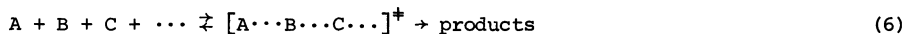
Table1. Sensitivity analysis—thermochemical estimates

Quantity	Uncertainty	Uncertainty in k or K (or other)
$\Delta S^{\circ}$ or $\Delta S^{\ddagger}$	$\pm 1$ e.u.	factor of 1.6 (x 1.6)
$\Delta H^{\circ}$ or $\Delta H^{\ddagger}$	$\pm 1$ kcal	x 5 (300 $^{\circ}$ K) x 1.6 (1000 $^{\circ}$ K)
	$\pm 0.3$ kcal	x 1.6 (300 $^{\circ}$ K) x 1.16 (1000 $^{\circ}$ K)
internal frequency	$\pm 20\%$	max. of $\pm 0.4$ e.u. in $S_T^{\circ}$ max. of $\pm 0.2$ e.u. in $C_{pT}^{\circ}$
bond length	$\pm 5\%$	max. of $\pm 0.2$ e.u. in $S_T^{\circ a}$ no direct effect on $C_{pT}^{\circ}$
bond angle	$\pm 5\%$	max. of 0.2 e.u. in $S_T^{\circ}$ no direct effect on $C_{pT}^{\circ}$

<sup>a</sup>In polyatomic molecules it is only the largest distances between the two or three heaviest atoms that are important in determining the moments of inertia.

#### Kinetic Parameters

Transition State Theory by separating equilibrium chemical reactions from processes determined by energy transfer has essentially reduced chemical kinetics to a thermochemical science. In equilibrium kinetics, there is a transition state (TS) which in equilibrium with reactants:



and the rate constant  $k_o$  can be written:

$$k_o = kT/h K^{\ddagger} \quad (7)$$

where the quantities in parentheses are known and  $K^{\ddagger}$  is the equilibrium constant describing the transition state. It has proven impossible to predict  $K^{\ddagger}$  from first principles but one

can use known experimental rate data for key reactions and deduce  $\Delta H_{f298}^{\ddagger}$  and  $S_{298}^{\ddagger}$  for transition states involved. From this it is possible to deduce values and empirical rules for predicting Arrhenius parameters for given elementary reactions (Ref.1). The relations are:

$$A = ekT_m/h \exp \{ \Delta S^{\ddagger}/R \} \quad (8)$$

$$E = \Delta H^{\ddagger} + RT \quad (9)$$

Where prior data exists it is possible to estimate A-factors to a factor of 2 and activation energies E to  $\pm 2$  kcal/mole. Where a rate measurement has been made at one temperature it is possible to estimate A better than it can usually be measured by extended temperature measurements.

Reaction rates dominated by energy transfer processes, such as atom recombination the dissociation of small molecules, electron fragmentation of molecules, and many ion-molecule reactions can be handled by combinations of transition state theory and what is now referred to as the RRKM Theory of non-equilibrium processes (Ref.3). Here too, empirical rules have been developed for assigning structural features to transition states and energy transfer rates for very highly, vibrationally-excited, species. A key distinction here has been between transition states characterized by very steep energy barriers on both sides (reactants and products) and those in which the barrier is steep on only one side (dissociation of diatomics). The former are termed "tight" transition states, the latter "loose" transition states. The loose TS resemble the separated species while tight TS are intermediate between reactants and products. Loose TS have essentially zero energy barrier on going to products. Tight TS have significant energy barriers on both sides.

For tight transition states the difference in activation energies (reactant or product side) is of course equal to the heat of reaction. The smaller of the two energies (i.e. in the exothermic direction) is labelled the "intrinsic" activation energy. It has been impossible to predict intrinsic activation energies with useful precision ( $< 2$  kcal) from first principles. However it is possible to predict them to  $\pm 1$  kcal using empirical rules and additivity laws (Ref.1).

#### Mechanism

One of the major obstacles historically, to the development of a complete foundation for chemical kinetics has been our uncertainty about the generic pathways of "mechanisms" for elementary reactions. We have today achieved very close to a complete accounting of mechanism, both for reactions in the gas phase and in condensed phases. What is meant by this, is that we have a semi-quantitative grasp of the energies and entropies associated with any structure one may write for a proposed transition state and hence may estimate, although crudely in many cases, the rate parameters associated with that path. No reaction is ever "forbidden." It may have a very high activation energy associated with it.

The constraints we must consider are:

1. Spin Conservation
2. Ring strain-ring entropy (cyclic structures)
3. Orbital symmetry conservation
4. Franck-Condon restrictions (electrons, radiation)

The first three of these are dominated by penalties of higher activation energies. The A-factor penalty for violating spin or orbital conservation is usually quite small. It will always involve a tight TS. For the formation of rings in the TS we pay a price both in ring strain energy and in ring entropy. The latter can involve factors of  $10^{-1}$  to  $10^{-3}$ . Franck-Condon restrictions can involve penalties in A-factors or activation energies or both. These are usually processes involving the very disparate motions of particles with very different masses. Changes in electronic dates and radiative interactions belong to this class. H atom motions in molecules may also show similar restraints.

Activation energy barriers in exothermic reactions usually arise from the requirement of promoting electrons from closed valence shells. Free radicals or atoms combine with no activation energy because we have an unpaired electron in one and an open orbital to receive it in the other. Only spin and steric restrictions modify the A-factors. These recombinations are characterized by loose TS. Metathesis reactions generally have activation energies in the range 0-15 kcal and occasionally in special cases, up to 25 kcal. These are generally atom-molecule or radical-molecule and have one species with an odd electron but the other closed shell. These require electronic promotion in only one species. Molecule-molecule reactions have intrinsic activation energies in the range 15-50 kcal and require two electronic promotions. In all of these we find quite remarkable correlations of observed E with electron affinities and polarizabilities (Ref.5) which give us reasonable confidence in estimating E for related species.

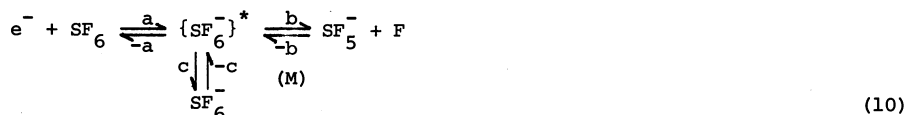
Ion-molecule reactions may have spin and orbital restrictions, but seldom activation

energies. The reason is that they parallel metathesis reactions and hence might be expected to have intrinsic activation energies in the 0-15 kcal range. However, the polarization interaction is generally larger than this and hence reduces the net requirement to zero. Most cross-sections are very close to the Langevin value.

### Energy Transfer Processes

These generally fall into two extreme classes. One is the exchange of energy to thermalized species from vibronic to translational and/or rotational modes. These are of interest in laser processes and in boundary layer relaxation and have been reasonably treated by both Landau-Teller and resonant models. The other class is vibronic energy transfer to and from highly internally excited species. These play a key role in the dissociation of small molecules and the inverse processes of recombination of atoms and small radicals. The efficiency of these latter processes is high in the range of 1 to  $10^{-2}$  per gas phase collision and has been found to correlate very closely, as might be expected, with intermolecular forces between collision partners (Ref.3). Modern treatments of ion fragmentation channels in mass spectrometry utilize RRKM theory very successfully in analyzing the molecular processes. The chief problems in making quantitative a priori assignments is the uncertainty of knowing the original energy depicted by the electron beam (seldom monochromatic) and the energy partition in the fragments. Also lacking is a reliable and broad knowledge of heats of formation of the fragment ions and metastables.

It is of interest to see how one might apply these techniques to the case of an electron-molecule reaction. Fehsenfeld has measured the rate of thermal electron capture by  $SF_6^-$  at 300-500°K and 0.2-1.5 torr (Ref.6). He found a value of  $2.2 \times 10^{-7}$  cc/particle-sec for what appears to be a strictly 2nd order process. He also found about 0.10% (300°K) and 5% (500°K) of  $SF_5^-$  formed, showing an apparent activation energy of 10 kcal. We can write for the reaction:



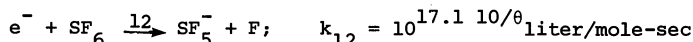
RRK theory (Ref.7), a simplified, older version of RRKM theory, gives as the condition that the rate be bimolecular.

$$k_c(M) > k_{-a} \approx A_{-10} \left[ \frac{E-E_0}{E} \right]^{s-1}$$
(11)

Where (M) = conc. of He or Ar, the carrier gas and  $k_c$  is the deactivation rate constant for excited  $SF_6^-\ast$ ,  $A_{-10}$  is the Arrhenius A-factor for the high pressure decomposition of thermal  $SF_6^-$ ,  $E_0$  is the electron affinity of  $SF_6^-$ ;  $s$  is the effective number of internal degrees of freedom of  $SF_6^-$  capable of exchanging energy ( $s = (C_p - 8)/R \leq 15$ ) and  $E - E_0$  is the thermal energy of  $SF_6^-$  at temperature.

If we assume that  $SF_6^-$  has the same symmetry and bond lengths as  $SF_6$  and roughly the same frequencies  $S_{300}^0(SF_6^-) = S_{300}^0(SF_6) + 1.4$  e.u. and  $\Delta S^0$  for reaction 10 is -3.6 e.u. From detailed balancing the Arrhenius A-factor for the thermal decomposition of  $SF_6^-$  is then,  $A_{-10} = A_{10} \exp(-\Delta S_{10}/R) = 1 \times 10^{13}$  sec $^{-1}$ . With  $s$  (300-500°K) = 10 + 1,  $(E - E_0) \approx 6.4$  kcal and  $k_c$  taken equal to collision cross-section  $\approx 1.5 \times 10^{-9}$  cc/p-sec =  $9 \times 10^{11}$  L/mole-sec, we find that  $M = 10^{15.8}$  p/cc,  $E_0 \geq 32$  kcal. From independent sources (Ref.6) this is also the observed electron affinity.

From the observations we can calculate for the process:



where  $\theta = 2.303 RT$  in kcal/mole. From the estimated  $\Delta S_{12} = 31.5$  e.u.,  $k_{-12} = 10^{10.4}$  l/mole-sec. This latter value is close to that estimated a priori for the loose TS, recombination reaction, if we assumed that  $SF_5^-$  has a square-planar pyramidal structure similar to octahedral  $SF_6$  with the electron occupying the space occupied by the missing F in the latter.

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