

# The Collision Theory of Chemical Reactions in Liquids



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LONDON: METHUEN & CO LTD  
NEW YORK: JOHN WILEY & SONS INC

*First published in 1964*  
*© 1964 by Alastair M. North*  
*Printed in Great Britain by*  
*Spottiswoode, Ballantyne & Co Ltd*  
*London and Colchester*

## Preface

Kinetic studies of chemical reactions are usually based upon either a Collision Theory or a Transition State Theory. Because an advanced level of understanding of the gaseous state has existed for several years, a number of excellent treatises have been published in which these chemical kinetic theories are discussed in terms of the well-known kinematic or thermodynamic properties of gaseous systems. Unfortunately the gain of knowledge concerning molecular energetics and the transport and collision processes in liquids has lagged behind the understanding of gaseous systems, with the consequence that derivation of a Collision Theory in liquids is considerably more difficult.

A most unfortunate consequence of this is that there exists a great temptation to draw conclusions from studies of chemical kinetics in liquid systems, using equations derived rigorously only for gaseous phases. Since a very large number of chemical reactions are most readily studied in liquid systems, and since quantitative theoretical implications are often drawn from such studies, it is essential that the effects of the transport and collision phenomena which are peculiar to liquids be appreciated and, if possible, be quantitatively calculable. In this volume the phrase 'Collision Theory of Reactions in Liquids' is taken as referring to any treatment of chemical reaction as a two-stage process (transport and reactant pair formation followed by chemical reaction) no matter how each of these stages be further discussed.

The current renaissance of interest in the application of modern collision theory can only extend to the liquid state if the scope and limitations of present knowledge are clearly realized, and it is unfortunately the case that a completely satisfactory collision theory of chemical reactions in liquids cannot yet be formulated. For this reason the most recent theories of transport and energy transfer in liquids are introduced in a qualitative (rather than a rigorously quantitative) fashion as the foundation upon which future developments of collision theories in liquids will probably be based.

The principal aim of this book has been to suggest how certain commonly used kinetic rate expressions might be modified so as to take account of the encounter phenomena peculiar to liquids. The text is, therefore, intended more as a guide for the practical chemist, faced with the task of interpreting or comparing various liquid-phase reaction rate constants, than as a complete theoretical discourse on the niceties of mass and energy transfer. For the sake of brevity, too, the discussion has been kept as general as possible, dealing principally with types of chemical reaction (e.g. slow ion-ion reactions or fast dipole-dipole reactions) rather than with the behaviour of individual chemical compounds. In view of the uncertainties inherent in the experimental measurement and in the theoretical comparison of reaction rates, this aim must be interpreted not as an attempt to expound a panacea for all mysterious rate variations, but as a warning against the facile explanation of all rate phenomena in terms of some 'perturbed' transition state.

The choice of material to be omitted in a book of this nature is always controversial, and the decision must eventually be a personal one reflecting the interests, and also the failings, of the author. It is hoped that those chemists who cannot agree with the vigorous pruning of the subject matter, or with the decided bias of the text towards attempting an interpretation of an 'observed' reaction rate constant despite all sorts of terrible assumptions, may still find some sections that provide interesting and enjoyable reading.

The author wishes to place on record his indebtedness to several of his colleagues, without whose helpful suggestions, comments and criticisms the book could not have been written. Professor C. H. Bamford and Dr A. Ledwith have provided invaluable criticism of the manuscript, and the information crystallized from discussions with Professor S. W. Benson and Dr J. N. Bradley forms a debt that cannot be repaid.

# Contents

<b>Preface</b>	<i>page vii</i>
<b>1 Fundamental Concepts</b>	<b>1</b>
Introduction	1
Molecular collisions and encounters in liquids	2
Encounter and chemical reaction as two consecutive processes	8
Elementary transition state theory of rate processes	10
Elementary collision theory of chemical reactions	14
<b>2 Diffusion and Mass Transport in Liquids</b>	<b>19</b>
General equations	19
Hole theory of diffusion in liquids	24
Statistical mechanical treatment of transport in liquids	30
Rotational diffusion and relaxation in liquids	32
<b>3 Simple Equilibrium Treatment of Chemical Reaction During an Encounter: Theory</b>	<b>37</b>
The equilibrium concentration of encounter-pairs	37
Collision frequency during an encounter	55
Vibrational relaxation in liquids	59
The steric factor	60
Overall rate of chemical reaction	61
<b>4 Kinetic Treatment of Reactant Encounters: Theory</b>	<b>65</b>
Simple application of Fick's laws to encounter formation	65
Diffusion and pair-probability distribution	69
The behaviour of molecular pairs	72
Collisions on pseudo-crystalline lattices	76
Corrections for long-range interactions	77

<b>5 Temperature-Dependence of Liquid-phase Rate Constants:</b>	
<b>Comparison with Transition State Theory</b>	<b>82</b>
Arrhenius activation energies	83
Arrhenius pre-exponential factors	88
Comparison of collision and transition state theories	92
Corresponding state treatment of a reaction in different solvents	96
The effect of pressure	97
<b>6 Application of the Rate Equations to Experimental Data</b>	<b>102</b>
Comparison of gas-phase and liquid-phase reactions	102
Fast reactions	105
Slow chemical reactions; non-polar reactants	109
Slow chemical reactions; polar reactants	111
<b>7 Some Special Encounter Phenomena</b>	<b>116</b>
Charge-transfer reactions	116
Reactions of polymeric molecules	126
‘Cage’ reactions	135

## CHAPTER 1

# Fundamental Concepts

### Introduction

The kinetic features of a chemical reaction are usually studied in order to elucidate the mechanism of the reaction and to yield information on the chemical nature and reactivity of the species taking part. The mechanism can often be inferred from the dependence of the reaction rate, or products, upon such parameters as reactant concentration, temperature, or pressure, no absolute value for a reaction rate constant being required. Evaluation of the reactivity of a chemical species, however, usually requires the assigning of an absolute value to a chemical reaction rate constant, or a comparison of the values obtained for a series of rate constants. If any significance is to be attached to comparisons of evaluated rate constants, it is essential that the importance of all the terms, which may be involved in the rate constant, be fully appreciated.

Chemical reactions which have been studied in gaseous systems have been treated theoretically from two fundamental points of view. The first treatment, based upon the Kinetic Theory of Gases, sets out to derive an expression for a reaction rate constant in terms of the number of molecular collisions between reactants, and the probability that any such collision will involve reactants possessing energy great enough to bring about chemical reaction. This Collision Theory, and various extensions such as that to cover unimolecular reactions, appears in many texts on chemical kinetics. The second standard treatment, the Transition State Theory, is based upon theories of rate processes (GLASSTONE, LAIDLER, EYRING 1941). Basically this treatment expresses a reaction rate constant in terms of the thermodynamic differences which exist between an initial reactant state and some state (of higher energy) intermediate between reactants and products. In their simpler forms both these theories allow the expression of a reaction rate constant as an exponential function, in which a mildly temperature dependent pre-exponential term is

multiplied by an exponential of the form  $\exp(-E_a/RT)$ .  $E_a$  is an activation energy, the exact significance of which need not be considered at this juncture,  $R$  is the gas constant and  $T$  the absolute temperature.

Treatments based upon the Collision Theory suggest that the pre-exponential term is a collision number, i.e. the number of collisions occurring in unit time at a gas density of one molecule (or mole) in unit volume. Calculated, and many observed values of this number are of the order of  $10^{-10}$  c.c. molecule $^{-1}$  second $^{-1}$  ( $10^{11}$  l. mole $^{-1}$  sec $^{-1}$ ) and this value has come to be considered a 'normal' pre-exponential factor for a bimolecular reaction. Unfortunately this value is often used as a criterion of 'normalcy' for reactions taking place in solution, where it is apparent that the collision processes might differ markedly from those in gases. Consequently it is essential to investigate the way in which the collision phenomena, which are characteristic of liquid systems, affect the Collision or Transition State Theories of Chemical Reactions.

### **Molecular Collisions and Encounters in Liquids**

From the viewpoint of chemical kinetics it is usual to consider that two molecules are in a state of collision when the intermolecular separation has so decreased that the interaction potential is one of strong short-range repulsion. This first simple statement then leads directly to the viewpoint that a collision is a situation whereby the total kinetic energy of the two molecules can be redistributed between them, and where the possibility exists for transfer between translational kinetic energy and energy stored in vibrational, rotational, or electronic modes. Although certain species, such as ions or molecular dipoles, require a more detailed description than afforded by this generalization, let us first examine some consequences of the simple picture.

Chemical reactions between uncharged particles usually involve the formation or breaking of chemical bonds. Consequently our study of collisions must place emphasis upon the possibility of changing the vibrational energy of a molecule. The interatomic bondings in a molecule can be considered as a series of coupled weakly anharmonic oscillators. The extent and efficiency of the coupling, of course, is often a matter for conjecture.



Whether or not an intermolecular collision alters the vibrational energy of a particular bond depends on the collision duration. If this duration has a magnitude similar to the period of a molecular vibration, the bonds to atoms involved in the actual repulsion of the collision will experience a compressing force and there will not be time for this force to be progressively distributed among the other atoms in the molecule. An efficient transfer of energy from translational modes to the vibrational modes of the atoms concerned is the result. On the other hand, if the collision duration extends over the time for many vibrations, the energy of the collision can be continuously distributed over all the coupled oscillators. Consequently the kinetic energy of the molecule as a whole is altered, and there is no marked change in the vibrational energy of particular bonds. This situation represents inefficient energy transfer between translational and vibrational modes. The length of time over which the collision extends depends upon the form of the interaction potential at the locus of contact. Quite generally, the steeper the interaction potential gradient, the shorter the time and distance required for redirection and separation of the colliding molecules. The interaction potential gradient at the 'turn-around' point is steepest when there is a strong attractive potential between the 'contact' atoms, as illustrated diagrammatically in Fig. 1.1, so that a strong interatomic attraction is associated with inefficient transfer. For bimolecular collisions in gases it is possible to use acceptable functions for the interaction potential and calculate the efficiency of a collision with respect to translation-vibration energy transfer (MONTROLL and SHULER 1958).

The importance of selecting a relevant collision diameter has recently been stressed by ROWLINSON (1961). From the viewpoint of chemical reaction a critical maximum separation of the molecules exists above which no reaction can take place. This separation need not be the same as the 'glancing-collision' diameter evaluated from gas viscosity or thermal conductivity. If the chemical critical separation lies in the region where the interaction potential is negative, slow-moving molecules are accelerated to this separation, and the number of collisions is greater than the number calculated for 'hard-spheres' by the factor,  $(1 - U(d)/kT)$  where  $U(d)$  is the interaction potential energy at the critical separation. On the other hand, if the critical

separation lies in the region where the interaction potential is positive, slow-moving molecules will be repelled before reaching the critical separation, reducing the collision number relative to 'hard-spheres' by the factor  $\exp(-U(d)/kT)$ . This latter case seems more realistic for those chemical reactions which involve a measurable activation energy, of which  $U(d)$  may constitute a part. The convenient, and

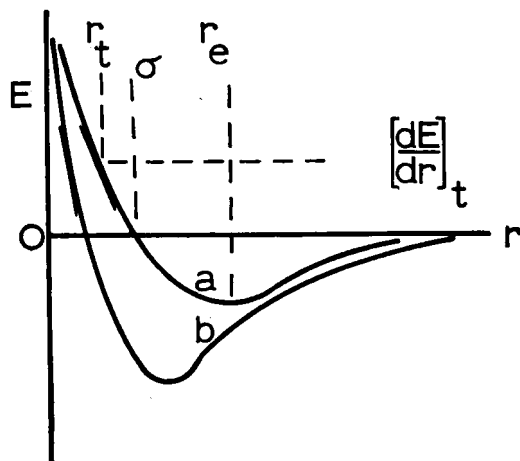


Fig. 1.1. Intermolecular collision parameters for two molecules: *a.* with weak intermolecular attraction, *b.* with strong intermolecular attraction.

much used, definition of a collision diameter as that separation corresponding to zero interaction potential can now be appreciated, since the number of such collisions is the same as the number undergone by hard spheres of the same collision diameter.

These considerations are especially important when a collision number is to be combined with the efficiency of collision with respect to translation-vibration energy transfer. In the more empirical treatments of chemical kinetics where one is concerned with the number of collisions involving a total energy greater than a certain critical energy,  $E$ , the energy  $U(d)$  at the critical separation can often be

included in the total energy,  $E$ . In this case a useful relationship has been derived by CARERI (1958). The significant diameter,  $d$ , of a collision from the viewpoint of an ensuing chemical reaction is related to the diameter,  $d_0$ , determined from transport experiments on the dilute gas at a temperature,  $T_0$ , by the equation

$$d = d_0(E/kT_0)^{-1/n}. \quad (1.1)$$

$n$  is the exponent of the repulsive term in the intermolecular potential,  $U(d) = \alpha/d^n$ , and  $E$  is the total activation energy of the chemical reaction. This collision diameter can then be inserted in the usual equations for calculating a collision number.

Whatever refinements are introduced, molecular collisions in gases can be described using the well-known equations of the kinetic theory in conjunction with certain terms relevant to the interactions occurring during the collision.

When collisions take place in liquid systems, there are two complicating factors. In the first place there is a distinct probability that any molecule undergoing 'collision' is, in fact, influenced by the interaction potentials of more than one other molecule. Secondly, many materials which are liquids at normal temperatures exhibit dipole-dipole or other strongly polarizing interactions. These factors make the calculation of realistic collision orbits extremely difficult, and consequently cause any *ab initio* computation of energy transfer efficiency to be of questionable value. On the other hand, they do not invalidate any chosen consideration of a collision diameter.

The fundamental reason, of course, for the high probability of ternary and higher order collisions is the close-packing (relative to a gas) of the molecules in a liquid. In fact the 'free-volume' of a liquid is less than the molecular volume, so that the distance separating the centres of neighbouring molecules must, on average, be less than two collision radii. This means that a molecule cannot pass between two others without experiencing an interaction which for most cases is strong repulsion. In other words the molecule requires a finite amount of energy to 'squeeze' between two others.

The principle of equipartition of energy applies to molecules in a liquid under the same equilibrium conditions as in a gas, so that any

reference average molecule will have translational movement. Because the mean free path is so short in a liquid (of the order of a molecular diameter), and because of the resistance to passage between other molecules, the collisions undergone by the reference molecule add up to a series of reflections. This fact allows us to consider the movement of the molecule as a vibration about a particular point in

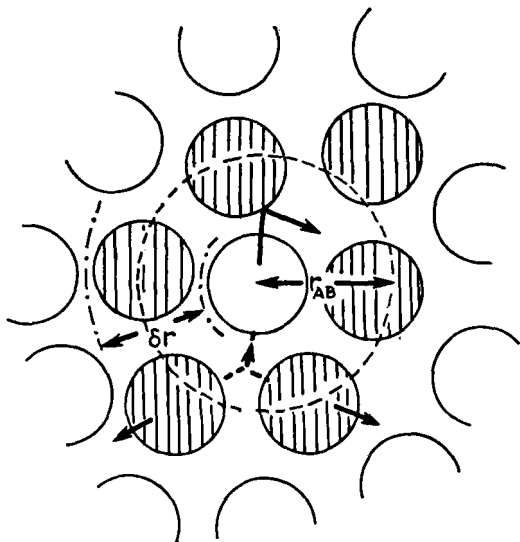


Fig. 1.2. Movement of a reference molecule in a liquid.

the liquid, as depicted in Fig. 1.2. This state of 'vibration' continues until it is possible for the molecule to pass between two neighbours. The lifetime,  $\tau$ , of this state can be related to the period of 'vibration',  $\tau_0$ , using the equation (FRENKEL 1946)

$$\tau = \tau_0 \exp(W/kT) \quad (1.2)$$

where  $W$  represents the increase in the free energy of the system (reference molecule and neighbours) which is required to permit escape of the 'vibrating' molecule. The free energy,  $W$ , has a value

greater than  $kT$  for most common liquids at room temperature, so that the reference molecule undergoes many collisions with a fixed set of neighbours or, of course, with any particular neighbour. When the reference molecule and a particular neighbour are chemical reactants, the phenomenon of repeated collision is often referred to as an 'encounter' within a solvent or liquid 'cage'. It is immediately apparent that diffusion of a molecule from point to point through a liquid is slower than through a gas. Then the number of encounters between reactants is smaller than the number of collisions between reactants of identical capture cross-section and concentration in the gas phase. On the other hand, the long duration (with repeated energy transfer) of any encounter raises the probability of chemical reaction considerably above that referring to the single collision dealt with in the simple treatment of gaseous reactions.

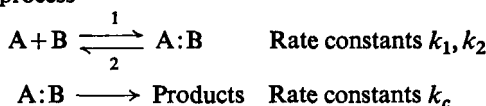
Before discussing the collision phenomena between two reference molecules in greater detail, it is necessary to appreciate the magnitude of the factors involved in an encounter. In the first place a molecular collision in the gas phase extends over a time of approximately  $3 \times 10^{-13}$  sec (COTTRELL and MCCOUBREY 1961), and there is no reason why the duration of a collision in a liquid should be greatly different. The molecular velocities in a liquid are of the order  $10^4$  to  $10^5$  cm/sec, and the mean free path is only a few ångström units. The 'vibration period',  $\tau_0$  is then  $10^{-13}$  to  $10^{-12}$  sec. Inverted commas are used to differentiate this molecular movement from the vibrations of the atoms in the molecule, and are not meant to dispute the consideration of reflected translation as a vibration. Since any system of moving molecules attains a Maxwell-Boltzmann distribution of molecular velocities in times comparable with the time required to complete a mean free path (JEANS 1925, BERNE 1953), for almost all practical purposes this velocity distribution can be assumed for molecules in a liquid (BORN and GREEN 1949). As we have already seen,  $\exp(W/kT)$  has a value which is often between  $10^2$  and  $10^4$ , leading to encounter lifetimes of  $10^{-10}$  to  $10^{-8}$  sec. For viscous liquids, of course, the encounter lifetimes may be much larger, and in the case of glasses may be several seconds, or indeed days. While considering plausible values of the free-energy increase,  $W$ , it is convenient to note that this is dependent upon the separation of the molecules in the liquid.

Consequently it is both pressure and temperature dependent, a fact which will be considered in greater detail in Chapter 5. The task of a Collision Theory must then be to describe the frequency of reactant encounters, and the number of collisions per encounter.

### Encounter and Chemical Reaction as Two Consecutive Processes

Since a pair of reactants undergoing an encounter remain in proximity for a finite time, the 'encounter-pair' can be considered as a transient intermediate in the conversion of reactants to products. The kinetic implications of this intermediate state of finite lifetime and finite concentration, can be perceived from a somewhat simplified illustration.

As in gaseous systems, an initial reactant state is characterized by a statistical separation of reactant molecules, with the possibility of an initial concentration of pairs. The separated reactants diffuse together to form 'encounter-pairs' which either react or break up into freely diffusing reactants. This can be written as a two-stage (transport and chemical) process



where A and B represent separated reactants and A:B the 'encounter-pair'. The simultaneous equations describing the time dependence of all the species involved do not yield a general explicit solution. There are two particular cases, however, which afford useful illustrations for our purpose. The first case arises when the concentrations of free reactants, A and B, are effectively constant. Under these conditions the differential equations can be solved to yield

$$\begin{aligned} [A:B] = [A:B]_0 \exp\{-(k_2 + k_c)t\} \\ + \frac{k_1[A]_0[B]_0}{k_2 + k_c} (1 - \exp\{-(k_2 + k_c)t\}) \end{aligned} \quad (1.3)$$

where the zero subscripts refer to conditions at the commencement of observations,  $t_0$  being zero. Any observed rate 'constant' defined by

$$\frac{d[\text{Products}]}{dt} = k_{\text{obs}}[A][B] \quad (1.4)$$

can then be evaluated as

$$k_{\text{obs}} = \frac{k_c[A:B]_0 \exp\{-(k_2 + k_c)t\}}{[A]_0[B]_0} + \frac{k_1 k_c}{k_2 + k_c} (1 - \exp\{-(k_2 + k_c)t\}) \quad (1.5)$$

This concentration- and time-dependent coefficient becomes at long times,

$$k_{\text{obs}} = \frac{k_1 k_c}{k_2 + k_c} \quad (1.6)$$

Whatever the relative magnitudes of  $k_2$  and  $k_c$ , rate coefficients descriptive of the transport processes appear in the expression for the observed rate constant. This long-time result could, of course, have been obtained as easily assuming a stationary-state concentration of A:B pairs.

The second case of interest occurs when the chemical reaction is sufficiently slow compared with the transport processes that the equilibrium concentration of A:B pairs is not sensibly perturbed by chemical reaction. This is a situation which applies to many chemical processes, and is the situation in which transport and collision phenomena are so often ignored. In this case we set  $[A:B] = K_{AB}[A][B]$  where the equilibrium constant can, if so desired, be related to the kinetic processes by  $K_{AB} = k_1/k_2$ . In this case the observed rate constant  $k_{\text{obs}}$ , is the product of a first-order rate constant and an equilibrium constant, which latter is a function of the collision phenomena of the solution or liquid system.

Both of these illustrations contain the implicit assumption that the concentration of reactants around the reaction loci can be described by the average concentration over the whole system. For fast reactions it is perfectly possible that there could arise a serious deficiency of reactant in this region, the removal of reactive species occurring more rapidly than the replacement from unreactive positions in the solution. In this case the apparent reactivity of the reactants will decrease with time, an effect which must always be borne in mind when considering fast reactions in liquid systems.

It readily becomes apparent that no matter what conditions are imposed upon the relative magnitudes of separate steps, a rate constant describing the overall process contains terms relating to pair-formation. It is sometimes argued that the Transition State Theory, being based upon the states of initial and maximum energy, should be independent of the encounter mechanism. This is not, of course, strictly true. A rigorous treatment of a process with more than one energy maximum treats the positions of minimum energy as *meta*-stable states, and examines the way in which changes in the population of these states affects the population of the so-called transition state. This is the same process as breaking a complete reaction into a series of consecutive steps. It is possible to apply Rate Process Theory to any or all of the reaction steps and, since the two-stage process is often loosely referred to as a 'Collision Treatment' rather than an 'Encounter Treatment', we thus have the interesting combination – a Transition State treatment of a Collision Theory of chemical reactions in liquids! In this volume the phrase 'Collision Theory of Reactions in Liquids' is taken as referring to any treatment of chemical reaction as a two-stage (transport and chemical) process, no matter how each of these stages be further discussed.

We are now in a position to make a more precise statement of the problems facing a Collision Theory of Reactions in Liquids. These may be stated as:

1. How does the concentration of 'encounter-pairs' depend on time and on the various properties of the liquid under investigation?
2. How does an observed reaction rate constant depend on the transport processes in the liquid?
3. What might be 'normal' values for observed reaction 'collision-numbers'?

### **Elementary Transition State Theory of Rate Processes**

Absolute reaction rate theory can be applied to any process which may be described as passage of a representative point along a reaction co-ordinate which necessitates the crossing of a potential barrier. The theory can thus be applied both to chemical reactions, in which case the energy barrier is the activation energy of the reaction, and the reaction coordinate is generalized co-ordinate in phase space,



and to diffusion when the reaction co-ordinate is a simple displacement co-ordinate. The rate of the process under examination can be obtained from the use of statistical mechanics to calculate the number of particles on top of the barrier which are, in the simple treatment, assumed to be in thermodynamic equilibrium with those in the initial state. This number is then combined with the rate of passage across the barrier in the correct direction.

In order to calculate the number of particles on top of the barrier it is necessary to consider an arbitrary range,  $\delta$ , in which region the top of the barrier can be considered flat. That part of the reaction co-ordinate described by  $\delta$  is known as the 'transition state'. The ratio of the number of particles,  $n^*$ , in the transition state, to the number,  $n$ , in the initial state, is given by

$$\frac{n^*}{n} = \frac{Q^*}{Q} \quad (1.7)$$

where  $Q^*$  and  $Q$  are the partition functions for the corresponding states. The partition function for the system in the transition state may be factorized so as to isolate the translational partition function for a particle moving in one dimension in the length,  $\delta$ , so

$$Q^* = Q'(2\pi\mu kT)^{1/2} \delta/h \quad (1.8)$$

where  $\mu$  is the reduced mass of the particle,  $k$  is the Boltzmann constant and  $h$  is Planck's constant. Both for chemical reaction and for diffusion the mean velocity,  $v$ , along the reaction co-ordinate at constant potential energy is

$$v = (kT/2\pi\mu)^{1/2} \quad (1.9)$$

so that the time,  $\tau'$ , required to pass through the distance,  $\delta$ , is

$$\tau' = \delta(2\pi\mu/kT)^{1/2} \quad (1.10)$$

Then the number of particles crossing the energy barrier in unit time is

$$w = \frac{n^*}{\delta} (kT/2\pi\mu)^{1/2} = n \frac{Q^* kT}{Qh} \quad (1.11)$$