The Transport Properties for NonPolar Gases

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Chapman and Cowling have related the coefficients of viscosity, diffusion, thermal diffusion, and heat conductivity to a set of integrals, $\Omega_n^{(l)}(T)$ involving the law of force between pairs of molecules. We have evaluated these integrals for $l=1$, $n=1, 2, 3$; $l=2$, $n=2, 3, 4, 5, 6$; $l=4$, $n=4$, assuming that the energy of attraction is inversely proportional to the sixth power of the separation and the energy of repulsion is inversely proportional to the twelfth power. This assumption is excellent for spherical non-polar molecules and a big improvement on the Sutherland assumption. The mathematical analysis was very difficult but the results are simple. The transport integrals are evaluated for all temperatures in terms of the maximum energy of interaction and the collision diameters. This gives a "corresponding states" relationship which should apply to extremely hot and extremely cold temperatures where good experimental data are not available. The molecular constants can be obtained very accurately from experimental viscosity data, and they agree with values previously obtained from equation of state data.

I. INTRODUCTION

THE general relationship between the transport properties of gases and the intermolecular forces has been known for a long time, the basic theory having been developed by Chapman, Enskog, and others. Chapman and Cowling[1] have expressed the transport coefficients in terms of a set of integrals which they call $\Omega^{(l)}(n)$. Up to this time the actual evaluation of these integrals and the calculation of the transport properties as functions of temperature have been accomplished only for a certain few simple molecular models, in which the laws of interaction are quite artificial and unrealistic. The role of the interaction law in determining the coefficient of viscosity is not too important; however, other properties, such as thermal diffusion, are exceedingly sensitive to the form of the potential.

In this report, the transport coefficients are evaluated, making use of a more realistic law of interaction. The form selected for the potential is the one which has proven very satisfactory in explaining the equation of state data for simple non-polar gases:

$$E(r) = 4\epsilon[-(r_o/r)^6 + (r_o/r)^{12}], \qquad (1)$$

in which $r =$ the separation between the molecules, $r_o =$ the separation for which the energy of interaction is zero (i.e., collision diameter for low velocity head-on collisions), $\epsilon =$ energy difference between the separated molecules and the molecules in the configuration for which they have the maximum energy of attraction. The inverse sixth-power form for the energy of attraction represents faithfully the induced dipole-induced dipole interaction between two non-polar molecules. The inverse twelfth-power form for the repulsive component is a rough approximation to the exponential form required from quantum-mechanical considerations. The values of ϵ and r_o are obtainable from equation of state data and second virial coefficients.

Using the potential function in Eq. (1), it is possible to derive an expression for the angle of deflection, χ, of two colliding molecules; the development of a formula for χ is straightforward and follows from standard dynamical considerations. But the integration of the particularly awkward hyper-elliptic integrals which result is a major problem. Each collision, and hence each value of χ, is characterized by two parameters: $K =$ the relative kinetic energy at large separations of the colliding molecules along the line of centers in units of ϵ [see Eq. (22)]. $\beta =$ distance of closest approach in units of r_o if there were no interaction between molecules [see Eq. (23)].

The reduced collision cross sections, $S^{(l)}(K)$,

[1] S. Chapman and T. G. Cowling, *Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Teddington, 1939).

968

are then determined by[2]

$$S^{(l)}(K) = 4 \bigg/ \left[2 - \frac{1+(-1)^l}{1+l} \right]$$

$$\times \int_0^\infty [1 - \cos^{(l)}\chi] \beta d\beta. \quad (2)$$

The functions, $S^{(l)}(K)$, are variously defined collision cross sections divided by πr_o^2, the latter being the cross section for rigid molecules of collision diameter r_c. Hence, for rigid spheres the values of the $S^{(l)}(K)$ are unity. The usual transport cross section corresponds to $l=2$; other kinetic theory properties require $l=1, 4$, etc.

Next the functions $W^{(l)}(n;x)$ are obtained from

$$W^{(l)}(n;x) = \frac{1}{8} \left[2 - \frac{1+(-1)^l}{1+l} \right] x^{n+2}$$

$$\times \int_0^\infty e^{-xK} K^{n+1} S^{(l)}(K) dK, \quad (3)$$

in which

$$x = \epsilon/kT, \quad (4)$$

where k is Boltzmann's constant. The $W^{(l)}(n;x)$ are related to the $\Omega^{(l)}(n)$ of Chapman and Cowling by

$$\Omega^{(l)}(n) = r_o^2 \left(\frac{2\pi kT}{\mu} \right)^{\frac{1}{2}} W^{(l)}(n;x). \quad (5)$$

The values of $W^{(l)}(n)$ for various values of kT/ϵ are presented in Table I. In Eq. (5), μ is the

reduced mass of the colliding molecules,

$$\mu = m_1 m_2 / (m_1 + m_2). \quad (6)$$

Here the m_1 and the m_2 are the molecular weights of the colliding molecules divided by Avogadro's number.

The mechanical accuracy of the $W^{(l)}(n;x)$ is of the order of one part in three hundred, but there are certain physical limitations to their validity. First of all, the calculations were made on the basis of classical mechanics, and therefore it is to be expected that quantum corrections must be added at the lowest temperatures. Secondly, the form for the energy of interaction is substantially correct but not precisely accurate —for example, the energy of repulsion between helium atoms should increase less rapidly than the inverse twelfth power of the separation. And finally, all of the collisions are supposed to be elastic—an assumption which is valid for the noble gases but not altogether true for polyatomic molecules where the transfer of energy from translation to rotations and vibrations sometimes takes place. This latter effect is of considerable importance with respect to heat conductivity but does not seem to affect viscosity.

The coefficient of viscosity, η, of a pure component can be written in the form:

$$\eta = (5/(8r_o^2))(\mu kT/(2\pi))^{\frac{1}{2}}[V/W^{(2)}(2)]. \quad (7)$$

Here V is a slowly varying function of kT/ϵ given in Table II. It can be expressed in terms of the Chapman and Cowling "b_{ij}" by the relation:

$$V = \left[1 + [b_{12}^2/(b_{11}b_{22} - b_{12}^2)] + \frac{b_{11}(b_{12}b_{23} - b_{22}b_{13})^2}{(b_{11}b_{22} - b_{12})^2(b_{11}b_{22}b_{33} + 2b_{12}b_{13}b_{23} - b_{12}^2b_{33} - b_{23}^2b_{11} - b_{13}^2b_{22})} \right]. \quad (8)$$

The values of the individual "b_{ij}" are also given in Table II. They are simply related to the $W^{(l)}(n;x)$ in the following manner:

$b_{11}/Q = 4W^{(2)}(2)$,
$b_{12}/Q = 7W^{(2)}(2) - 2W^{(2)}(3)$,
$b_{22}/Q = (301/12)W^{(2)}(2) - 7W^{(2)}(3) + W^{(2)}(4)$,
$b_{13}/Q = (63/8)W^{(2)}(2)$
$\qquad - (9/2)W^{(2)}(3) + \frac{1}{2}W^{(2)}(4)$,
$b_{23}/Q = (1365/32)W^{(2)}(2) - (321/16)W^{(2)}(3)$
$\qquad + (25/8)W^{(2)}(4) - \frac{1}{4}W^{(2)}(5)$,
$b_{33}/Q = [(25137/256)W^{(2)}(2) - (1755/32)W^{(2)}(3)$
$\qquad + (381/32)W^{(2)}(4) - (9/8)W^{(2)}(5)$
$\qquad + (1/16)W^{(2)}(6) + \frac{1}{2}W^{(4)}(4)]$,

$\quad (9)$

in which

$$Q = r_o^2 (2\pi kT/\mu)^{\frac{1}{2}}.$$

In a similar way, the coefficient of thermal conductivity, λ, may be written:

$$\lambda = [c_v + (9/4)(k/m_1)](5/8r_o^2)$$
$$\times (\mu kT/2\pi)^{\frac{1}{2}}(H/W^{(2)}(2)). \quad (10)$$

Here c_v is the specific heat per gram of the gas.

[2] The $S^{(l)}(K)$ are simply related to the Chapman and Cowling functions, $\phi^{(l)}$, by the equation

$$S^{(l)}(K) = 4\phi^{(l)}/gr_o^2[2 - \{1+(-1)^l\}/(l+1)].$$

Here g is the initial velocity along the line of centers.

TABLE I. Collision integrals.

kT/ϵ	$W^1(1)$	$\Omega^{(l)}(n) = r_0{}^2 [2\pi kT/\mu]^{\frac{1}{2}} W^{(l)}(n)$ $W^1(2)$	$W^1(3)$	$W^2(2)$	$W^2(3)$	$W^2(4)$	$kT/\epsilon = 1/x$ $W^2(5)$	$W^2(6)$	$W^4(4)$
0.3	1.331	3.384	11.77	2.785	10.14	46.66	258.3	1672.0	61.36
0.35	1.238	3.117	10.77	2.628	9.498	43.26	237.4	1528.0	57.06
0.4	1.159	2.896	9.976	2.492	8.927	40.32	220.0	1413.0	53.36
0.45	1.092	2.712	9.333	2.368	8.419	37.78	205.6	1322.0	50.17
0.5	1.033	2.557	8.809	2.257	7.968	35.62	193.7	1248.0	47.41
0.55	0.9829	2.427	8.377	2.156	7.570	33.77	183.9	1189.0	45.01
0.6	0.9383	2.315	8.016	2.065	7.222	32.19	175.6	1139.0	42.92
0.65	0.8991	2.218	7.711	1.982	6.915	30.84	168.7	1098.0	41.09
0.7	0.8644	2.135	7.452	1.908	6.645	29.67	162.9	1064.0	39.49
0.75	0.8335	2.062	7.228	1.841	6.407	28.67	157.8	1034.0	38.09
0.8	0.8058	1.998	7.033	1.780	6.195	27.78	153.4	1009.0	36.83
0.85	0.7809	1.942	6.862	1.725	6.006	27.00	149.6	986.9	35.72
0.9	0.7585	1.892	6.711	1.675	5.838	26.32	146.3	967.5	34.73
0.95	0.7382	1.847	6.577	1.629	5.686	25.71	143.3	950.3	33.84
1.0	0.7197	1.806	6.456	1.587	5.550	25.16	140.7	935.0	33.04
1.05	0.7028	1.769	6.347	1.549	5.426	24.67	138.3	921.1	32.32
1.1	0.6873	1.736	6.248	1.514	5.315	24.23	136.2	908.8	31.66
1.15	0.6731	1.706	6.159	1.482	5.214	23.84	134.3	897.5	31.06
1.2	0.6601	1.678	6.077	1.452	5.121	23.47	132.5	887.2	30.52
1.25	0.6479	1.653	6.001	1.424	5.036	23.14	130.9	877.8	30.02
1.3	0.6367	1.629	5.932	1.399	4.957	22.84	129.4	869.1	29.57
1.35	0.6263	1.608	5.868	1.375	4.885	22.56	128.1	861.1	29.15
1.4	0.6166	1.588	5.808	1.353	4.819	22.30	126.8	853.6	28.76
1.45	0.6075	1.569	5.753	1.333	4.757	22.06	125.6	846.7	28.40
1.5	0.5991	1.551	5.701	1.314	4.699	21.83	124.5	840.1	28.06
1.55	0.5912	1.535	5.652	1.296	4.646	21.62	123.5	834.0	27.75
1.6	0.5837	1.520	5.607	1.279	4.596	21.43	122.6	828.2	27.46
1.65	0.5767	1.506	5.563	1.264	4.549	21.25	121.7	822.8	27.19
1.7	0.5701	1.492	5.523	1.248	4.505	21.08	120.8	817.7	26.93
1.75	0.5639	1.479	5.485	1.234	4.464	20.92	120.0	812.9	26.69
1.8	0.5580	1.467	5.449	1.221	4.425	20.76	119.3	808.3	26.47
1.85	0.5523	1.456	5.414	1.209	4.388	20.62	118.5	803.8	26.25
1.9	0.5471	1.445	5.381	1.197	4.353	20.48	117.9	799.7	26.05
1.95	0.5421	1.435	5.350	1.186	4.321	20.35	117.2	795.7	25.86
2.0	0.5373	1.425	5.320	1.175	4.290	20.23	116.6	791.9	25.68
2.1	0.5284	1.407	5.265	1.156	4.218	20.00	115.4	784.8	25.35
2.2	0.5203	1.390	5.213	1.138	4.179	19.79	114.3	777.9	25.04
2.3	0.5129	1.375	5.167	1.122	4.131	19.60	113.4	772.0	24.77
2.4	0.5061	1.361	5.123	1.107	4.087	19.42	112.5	766.1	24.51
2.5	0.4998	1.348	5.082	1.093	4.047	19.26	111.6	760.9	24.28
2.6	0.4939	1.336	5.044	1.081	4.009	19.11	110.8	755.7	24.06

The factor in the first parenthesis is the "Eucken correction" for the heat conductivity of molecules with internal degrees of freedom.[3] The rigorous kinetic theory is only intended to apply to the noble gases for which $c_v = 3k/2m_1$. The factor, H, is a slowly varying function of kT/ϵ, given in Table III. It can be expressed in terms of the Chapman and Cowling "a_{ij}":

$$H = \left[1 + [a_{12}{}^2/(a_{11}a_{22} - a_{12}{}^2)] + \frac{a_{11}(a_{12}a_{23} - a_{22}a_{13})^2}{(a_{11}a_{22} - a_{12}{}^2)(a_{11}a_{22}a_{33} + 2a_{12}a_{13}a_{23} - a_{11}a_{23}{}^2 - a_{22}a_{13}{}^2 - a_{33}a_{12}{}^2)} \right]. \quad (11)$$

The values of the individual "a_{ij}" are also given in Table III. They are simply related to the $W^{(l)}(n,x)$ in the following manner:

$$a_{11} = b_{11}, \quad a_{12} = b_{12}, \quad a_{13} = b_{13},$$
$$a_{22}/Q = (77/4) W^{(2)}(2) - 7 W^{(2)}(3) + W^{(2)}(4), \quad (12)$$

$$a_{23}/Q = (945/32) W^{(2)}(2) - (261/16) W^{(2)}(3) + (25/8) W^{(2)}(4) - \tfrac{1}{4} W^{(2)}(5), \quad (13)$$

$$a_{33}/Q = [(14553/256) W^{(2)}(2) - (1215/32) W^{(2)}(3) + (313/32) W^{(2)}(4) - (9/8) W^{(2)}(5) + (1/16) W^{(2)}(6) + \tfrac{1}{6} W^{(4)}(4)]. \quad (14)$$

[3] C. F. Curtiss and J. O. Hirschfelder, *The Kinetic Theory of Multicomponent Systems of Gases* (University of Wisconsin, Madison, July 1947), CF-727. Here an attempt is made to derive this factor but its validity is somewhat questionable.

The equations for the viscosity and thermal conductivity of a pure component can be written in the convenient forms:

TABLE I.—*Continued.*

kT/ϵ	$W^1(1)$	$\Omega^{(l)}(n)=r_o{}^2[2\pi kT/\mu]^{\frac{1}{2}}W^{(l)}(n)$ $W^1(2)$	$W^1(3)$	$W^2(2)$	$W^2(3)$	$W^2(4)$	$kT/\epsilon=1/x$ $W^2(5)$	$W^2(6)$	$W^4(4)$
2.7	0.4885	1.325	5.008	1.069	3.974	18.97	110.1	751.0	23.86
2.8	0.4836	1.315	4.974	1.058	3.942	18.83	109.4	746.5	23.67
2.9	0.4788	1.305	4.942	1.048	3.912	18.71	108.7	742.2	23.50
3.0	0.4745	1.296	4.912	1.039	3.883	18.59	108.1	738.2	23.33
3.1	0.4703	1.287	4.883	1.030	3.857	18.48	107.5	734.3	23.18
3.2	0.4664	1.278	4.856	1.022	3.831	18.37	106.9	730.6	23.03
3.3	0.4628	1.271	4.829	1.014	3.807	18.27	106.4	727.1	22.89
3.4	0.4593	1.263	4.804	1.007	3.785	18.17	105.9	723.8	22.76
3.5	0.4560	1.256	4.780	0.9999	3.763	18.08	105.4	720.5	22.64
3.6	0.4529	1.249	4.757	0.9932	3.743	17.99	104.9	717.3	22.52
3.7	0.4499	1.243	4.735	0.9870	3.723	17.91	104.4	714.3	22.40
3.8	0.4471	1.236	4.714	0.9811	3.705	17.83	104.0	711.4	22.29
3.9	0.4444	1.230	4.693	0.9755	3.687	17.75	103.6	708.6	22.19
4.0	0.4418	1.225	4.674	0.9700	3.670	17.68	103.1	705.9	22.09
4.1	0.4394	1.219	4.655	0.9649	3.653	17.61	102.7	703.2	22.00
4.2	0.4370	1.214	4.636	0.9600	3.637	17.54	102.4	700.7	21.90
4.3	0.4347	1.209	4.618	0.9553	3.622	17.47	102.0	698.2	21.81
4.4	0.4326	1.204	4.601	0.9507	3.607	17.41	101.6	695.8	21.73
4.5	0.4305	1.199	4.584	0.9464	3.594	17.34	101.3	693.5	21.65
4.6	0.4284	1.194	4.568	0.9422	3.580	17.28	100.9	691.2	21.57
4.7	0.4265	1.190	4.551	0.9382	3.567	17.22	100.6	689.0	21.49
4.8	0.4246	1.186	4.536	0.9343	3.554	17.17	100.3	686.8	21.42
4.9	0.4228	1.181	4.521	0.9305	3.542	17.11	99.99	684.8	21.34
5.0	0.4211	1.177	4.506	0.9269	3.529	17.06	99.68	682.7	21.27
6	0.4062	1.141	4.377	0.8963	3.426	16.59	97.00	664.6	20.67
7	0.3948	1.113	4.272	0.8727	3.344	16.21	94.82	649.8	20.19
8	0.3856	1.089	4.184	0.8538	3.277	15.89	92.99	637.3	19.79
9	0.3778	1.069	4.108	0.8379	3.219	15.62	91.40	626.5	19.46
10	0.3712	1.052	4.041	0.8242	3.169	15.38	90.01	617.0	19.17
20	0.3320	0.9439	3.629	0.7432	2.864	13.90	81.40	558.0	17.38
30	0.3116	0.8863	3.408	0.7005	2.700	13.11	76.75	526.2	16.42
40	0.2980	0.8477	3.259	0.6718	2.590	12.57	73.62	504.6	15.77
50	0.2878	0.8188	3.149	0.6504	2.507	12.17	71.28	488.6	15.28
60	0.2798	0.7960	3.060	0.6335	2.442	11.86	69.41	475.8	14.90
70	0.2732	0.7772	2.988	0.6194	2.388	11.59	67.88	465.3	14.58
80	0.2676	0.7613	2.927	0.6076	2.342	11.37	66.58	456.4	14.31
90	0.2628	0.7476	2.874	0.5973	2.302	11.18	65.45	448.7	14.08
100	0.2585	0.7354	2.828	0.5882	2.268	11.01	64.45	441.9	13.87
200	0.2322	0.6605	2.540	0.5320	2.051	9.956	58.29	399.6	12.59
300	0.2180	0.6203	2.385	0.5016	1.934	9.388	54.96	376.8	11.89
400	0.2085	0.5932	2.281	0.4811	1.855	9.004	52.72	361.4	11.42

$$\eta = 2.6693 \times 10^{-5} (MT)^{\frac{1}{2}} (r_o(\text{A}))^{-2}$$
$$\times (V/W^{(2)}(2)) \quad \text{(g/cm-sec.),} \quad (7')$$
$$\lambda = 2.6693 \times 10^{-5} (T/M)^{\frac{1}{2}} (r_o(\text{A}))^{-2}$$
$$\times (H/W^{(2)}(2))(C_v + (9/4)R)$$
$$\text{(cal./cm-sec.-deg.).} \quad (10')$$

In Eqs. (7') and (10') M is the molecular weight; $r_o(\text{A})$ is the low velocity collision diameter in angstroms; C_v is the specific heat in cal./mole deg., and R is the gas constant expressed in the same units.

The transport properties for gaseous mixtures can also be expressed in terms of the same collision integrals. The three parameters most useful in this connection are (using Chapman and Cowling notation):

$$A = W^{(2)}(2)/[5W^{(1)}(1)], \quad (15)$$

$$B = [5W^{(1)}(2) - W^{(1)}(3)]/[5W^{(1)}(1)], \quad (16)$$
$$C = 2W^{(1)}(2)/[5W^{(1)}(1)]. \quad (17)$$

The values of A, B, and C are given in Table IV. The viscosity, heat conductivity, diffusion, and thermal diffusion in mixtures can be determined for any particular case, but the formulas are not suited to any simple tabulations.

In order to use the collision integrals for any practical purposes, it is necessary to know the values of ϵ/k and r_o. Up to now they have been determined from experimental measurements of the second virial coefficient at two different temperatures. In a few cases they have been determined from the specific volume and compressibility of crystals. As a result of Eq. (7'), these constants can also be determined from measure-

TABLE II. Viscosity.

kT/ϵ	b_{11}/Q	b_{12}/Q	$\eta = 2.6693 \times 10^{-5}(MT)^{\frac{1}{2}}(r_0(A))^{-2}[V/W^{(2)}(2)]$ (g/cm-sec.) b_{22}/Q	b_{13}/Q	b_{23}/Q	b_{33}/Q	V	$V/W^{(2)}(2)$
0.30	11.14	−0.79	45.54	−0.37	−3.4	117.5	1.0014	0.3596
0.50	9.028	−0.14	36.46	−0.27	−0.7	92.5	1.0002	0.4432
0.75	7.364	+0.07	30.00	0.00	+0.1	76.9	1.0000	0.5432
1.00	6.348	+0.01	26.12	0.10	−0.2	67.7	1.0000	0.6301
1.25	5.696	−0.10	23.61	0.12	−0.7	61.8	1.0001	0.7023
1.5	5.256	−0.200	21.90	0.12	−1.13	57.7	1.0004	0.7613
2.0	4.700	−0.355	19.67	0.06	−1.88	52.1	1.0014	0.8523
2.5	4.372	−0.443	18.35	0.03	−2.28	48.8	1.0025	0.9172
3.0	4.156	−0.493	17.47	0.00	−2.51	46.6	1.0034	0.9657
4.0	3.880	−0.550	16.32	−0.04	−2.78	43.6	1.0049	1.036
5.0	3.708	−0.570	15.61	−0.05	−2.87	41.8	1.0058	1.085
10.0	3.297	−0.569	13.87	−0.08	−2.86	37.1	1.0075	1.222
50.0	2.602	−0.461	10.94	−0.07	−2.34	29.3	1.0079	1.550
100.0	2.353	−0.419	9.89	−0.07	−2.12	26.5	1.0080	1.714
400.0	1.924	−0.342	8.09	−0.057	−1.74	21.7	1.0080	2.095

ments of viscosity as a function of temperature. The experimental technique for measuring viscosity of gases has been perfected to such a degree that the experimental errors are less than our intrinsic computational errors of one part in three hundred. This accuracy is considerably better than can be obtained for second virial coefficients. This means that the experimental measurements of viscosity provide a superior means for determining the intermolecular force constants.

The experimental viscosity measurements of Herrick Johnston and his colleagues for twelve common gases at various temperatures are shown in Table V. By adjusting the constants, ϵ/k and r_0, and using Eq. (7′) we obtained the calculated values given in this same table. These constants can be compared with those previously obtained from an analysis of second virial coefficient data;

TABLE III. Thermal conductivity.

$\lambda = 2.6693 \times 10^{-5}(T/M)^{\frac{1}{2}}(r_0(A))^{-2}$
$\times [H/W^{(2)}(2)] \{C_v + (9/4)R\}$ (cal./cm-sec.-deg.)

kT/ϵ	a_{22}/Q	a_{23}/Q	a_{33}/Q	H	$H/W^2(2)$	H/V
0.30	29.29	−1.9	53.8	1.0022	0.3599	1.0008
0.50	23.29	−0.4	42.2	1.0003	0.4432	1.0001
0.75	19.26	0.0	35.3	1.0000	0.5432	1.0000
1.00	16.86	−0.2	31.2	1.0001	0.6302	1.0001
1.25	15.30	−0.5	28.7	1.0002	0.7024	1.0001
1.5	14.23	−0.75	26.9	1.0006	0.7615	1.0002
2.0	12.82	−1.21	24.4	1.0021	0.8529	1.0007
2.5	11.97	−1.45	22.9	1.0038	0.9184	1.0013
3.0	11.41	−1.59	21.9	1.0052	0.9675	1.0018
4.0	10.66	−1.75	20.5	1.0076	1.039	1.0027
5.0	10.20	−1.80	19.6	1.0090	1.089	1.0032
10.0	9.06	−1.80	17.5	1.0116	1.227	1.0041
50.0	7.14	−1.48	13.7	1.0124	1.557	1.0045
100.0	6.46	−1.34	12.4	1.0125	1.721	1.0045
400.0	5.28	−1.10	10.2	1.0125	2.105	1.0045

this comparison is made in Table VI. Some of the discrepancies are shockingly large, but in each of these cases the disagreement is less than the uncertainty of the constants determined from second virial data. The agreement between the calculated and the experimental viscosities in Table V is excellent for the following gases:

air, H_2, N_2, CO_2, N_2O, NO, and CH_4.

The agreement is only fair for

O_2, CO, and A.

The agreement is unsatisfactory in the cases of

Ne and He.

The poor agreement for helium should be expected, because theoretical considerations have shown that helium atoms are considerably less rigid than the inverse twelfth-power energy of repulsion would indicate; also, quantum corrections may be important at the lower temperatures.

The coefficient of diffusion, to the first approximation, depends only on collisions between unlike molecules. The temperature variation of the experimental coefficients of diffusion can therefore be used to determine the minimum energy of interaction, ϵ_{12}, and the collision diameter, $(r_0)_{12}$, between unlike molecules with considerable accuracy. The determination of these constants will be considered in a subsequent report.

II. DETAILED DISCUSSION OF DERIVATIONS AND CALCULATIONS

A. The Dynamics of a Collision

The energy of interaction between colliding molecules, $E(r)$, is assumed to have the form

given in Eq. (1) with an energy of attraction varying as the inverse sixth power and the energy of repulsion varying as the inverse twelfth power of the separation. Since this corresponds to a radial law of force, it is possible to express the trajectories in the form of well-known quadratures. These quadratures cannot be expressed in analytical form and must be evaluated by numerical procedures.

Kirkwood[4] has considered the effect of collisions in which the relative kinetic energy is not sufficient to permit the molecules to separate completely. The trajectories of these "bound molecules" are periodic with orbits large compared to molecular dimensions. Kirkwood showed that such collisions do not contribute to the

transport properties. In an ionic gas in which the energy of interaction varies as the inverse first power of the separation, there are a large number of "bound molecules." Since the number of molecules in a spherical shell of thickness dr at a distance r varies as r^2, if $E(r)$ decreases more rapidly than r^{-2} the fraction of "bound molecules" is small. In our case, at large distances $E(r)$ varies as r^{-6}, and the number of "bound molecules" is negligible. However, for very low energy encounters we sometimes obtain trajectories in which the molecules circle about each other for a few times at a distance of a few angstroms and separate of their own accord. In this respect they differ from Kirkwood's "bound molecules," which require the influence of a third molecule to effect the separation. Our examples of close orbiting correspond to well

TABLE IV. Constants for determination of transport properties of gaseous mixtures.

kT/ϵ	A	B	C
0.3	0.4185	0.7739	1.017
0.35	0.4246	0.7779	1.007
0.4	0.4300	0.7772	0.9995
0.45	0.4337	0.7742	0.9934
0.5	0.4370	0.7698	0.9901
0.55	0.4387	0.765	0.9877
0.6	0.4402	0.759	0.9869
0.65	0.4409	0.752	0.9868
0.7	0.4415	0.746	0.9880
0.75	0.4418	0.740	0.9896
0.8	0.4418	0.734	0.9918
0.85	0.4418	0.729	0.9947
0.9	0.4417	0.725	0.9978
0.95	0.4413	0.720	1.001
1.00	0.4410	0.715	1.004
1.05	0.4408	0.711	1.007
1.10	0.4406	0.707	1.010
1.15	0.4404	0.705	1.014
1.20	0.4399	0.701	1.017
1.25	0.4396	0.696	1.021
1.30	0.4395	0.695	1.023
1.35	0.4391	0.694	1.027
1.40	0.4389	0.692	1.030
1.45	0.4388	.689	1.033
1.50	0.4387	0.687	1.036
1.55	0.4384	0.684	1.039
1.60	0.4382	0.683	1.042
1.65	0.4384	0.682	1.045
1.70	0.4378	0.679	1.047
1.75	0.4377	0.677	1.049
1.80	0.4376	0.676	1.052
1.85	0.4377	0.676	1.054
1.90	0.4376	0.674	1.056
1.95	0.4376	0.673	1.059
2.00	0.4374	0.671	1.061
2.1	0.4375	0.670	1.065
2.2	0.4374	0.670	1.069
2.3	0.4375	0.666	1.072
2.4	0.4375	0.665	1.076
2.5	0.4374	0.664	1.079
2.6	0.4377	0.663	1.082

[4] John G. Kirkwood, J. Chem. Phys. **15**, 72 (1947).

TABLE IV.—*Continued.*

kT/ϵ	A	B	C
2.7	0.4377	0.662	1.085
2.8	0.4376	0.662	1.088
2.9	0.4378	0.661	1.090
3.0	0.4379	0.661	1.093
3.1	0.4380	0.660	1.095
3.2	0.4383	0.658	1.096
3.3	0.4382	0.659	1.099
3.4	0.4385	0.658	1.100
3.5	0.4386	0.658	1.102
3.6	0.4386	0.657	1.103
3.7	0.4388	0.658	1.105
3.8	0.4389	0.656	1.106
3.9	0.4389	0.656	1.107
4.0	0.4391	0.657	1.109
4.1	0.4392	0.655	1.110
4.2	0.4393	0.656	1.111
4.3	0.4395	0.656	1.112
4.4	0.4395	0.656	1.113
4.5	0.4396	0.656	1.114
4.6	0.4398	0.655	1.115
4.7	0.4399	0.656	1.116
4.8	0.4400	0.656	1.117
4.9	0.4402	0.655	1.117
5.0	0.4402	0.655	1.118
6	0.4413	0.656	1.125
7	0.4421	0.655	1.128
8	0.4428	0.657	1.131
9	0.4435	0.655	1.132
10	0.4441	0.657	1.134
20	0.4477	0.6569	1.137
30	0.4496	0.6569	1.138
40	0.4508	0.6574	1.138
50	0.4520	0.6567	1.138
60	0.4528	0.6569	1.138
70	0.4535	0.6574	1.138
80	0.4540	0.6573	1.138
90	0.4546	0.6575	1.138
100	0.4551	0.6569	1.138
200	0.4582	0.6568	1.138
300	0.4602	0.6573	1.138
400	0.4615	0.6571	1.138

TABLE V. Viscosity, η (in units 10^{-7} grams/cm-sec.).

$T(°K)$	Air $\epsilon/k=97.0$ $r_0=3.617$		H$_2$ $\epsilon/k=33.3$ $r_0=2.968$		N$_2$ $\epsilon/k=91.46$ $r_0=3.681$		CO$_2$ $\epsilon/k=190$ $r_0=3.996$		N$_2$O $\epsilon/k=220$ $r_0=3.879$		NO $\epsilon/k=119$ $r_0=3.470$	
	η_{exp}[a]	η_{calc}	η_{exp}[a]	η_{calc}	η_{exp}[a]	η_{calc}	η_{exp}[a]	η_{calc}	η_{exp}[a]	η_{calc}	η_{exp}[a]	η_{calc}
80												
100	713	702	421	416	698	687						
120	846	840	481	477	826	820					844	841
140	975	972	535	533	948	947					981	980
160	1101	1099	585	586	1068	1070					1115	1116
180	1221	1221	634	635	1183	1186			898	898	1245	1246
200	1336	1337	681	683	1295	1296	1015	1014	999	998	1371	1371
220	1448	1447	727	728	1403	1402	1112	1114	1099	1100	1493	1492
240	1556	1554	771	773	1505	1503	1209	1212	1198	1199	1610	1608
260	1659	1657	814	815	1603	1600	1303	1308	1296	1297	1711	1719
280	1756	1756	856	856	1696	1693	1400	1402	1393	1394	1838	1828
293.16	1819[b]	1819										
300	1851	1851	896	896	1786	1785	1495	1495	1489	1489	1934	1935
400	2294[d] / 2342[f]	2290	1127[f]	1073	2270[f]	2202	2015[f]	1923				
500	2680[d] / 2740[f]	2678	1305[f]	1237	2657[f]	2570	2450[f]	2309				
800	3613[d] / 3763[f]	3680	1744[f]	1689	3493[d] / 3610[f]	3528	3391[d] / 3567[f]	3285				
1000	4165[d] / 4349[f]	4257	1987[f]	1958	4011[d] / 4066[f]	4068	3935[d] / 4198[f]	3839				
1200	4631[d] / 4869[f]	4761	2205[f]	2199	4452[d] / 4613[f]	4554	4453[d] / 4766[f]	4348				
1500	5262[d] / 5524[f]	5494	2496[f]	2542	5050[d] / 5247[f]	5268	5139[d] / 5529[f]	5052				
5,000		12080										
10,000		18870										

$T(°K)$	CH$_4$ $\epsilon/k=136.5$ $r_0=3.822$		O$_2$ $\epsilon/k=113.2$ $r_0=3.433$		CO $\epsilon/k=110.3$ $r_0=3.590$		Argon $\epsilon/k=124.0$ $r_0=3.418$		Neon $\epsilon/k=35.7$ $r_0=2.80$		Helium $\epsilon/k=6.03$ $r_0=2.70$	
	η_{exp}[a]	η_{calc}	η_{exp}[a]	η_{calc}	η_{exp}[c]	η_{calc}	η_{exp}[c]	η_{calc}	η_{exp}[c]	η_{calc}	η_{exp}[c]	η_{calc}
80					533	523	688	649	1198	1212	821	827
100	403	393	768	757	669	657	839	814	1435	1451	947	957
120	478	472	917	910	796	788	993	979	1646	1665	1068	1086
140	560	553	1061	1059	919	916	1146	1142	1841	1867	1182	1197
160	629	630	1202	1203	1038	1040	1298	1300	2026	2054	1290	1305
180	703	707	1341	1342	1154	1160	1447	1454	2204	2231	1395	1413
200	778	780	1476	1474	1268	1274	1594	1601	2376	2396	1496	1509
220	850	852	1604	1602	1379	1384	1739	1744	2544	2558	1595	1605
240	919	921	1728	1726	1486	1489	1878	1882	2708	2713	1692	1700
260	986	987	1845	1845	1589	1591	2014	2014	2867	2862	1789	1789
280	1053	1052	1958	1959	1688	1689	2145	2143	3021	3008	1888	1877
300	1116	1116	2071	2070	1785	1784	2270	2269	3173	3149	1987	1964
400	1453[f]	1405	2644[f]	2578	2235[f]	2219						
500	1729[f]	1661	3112[f]	3031	2608[f]	2607						
800	2421[f]	2312	4115[e] / 4273[f]	4183	3529[f]	3595	4621[d]	4641	5918[e]	5945	3840[e]	3665
1000	2806[f]	2687	4720[e] / 4917[f]	4853	4040[f]	4168	5302[d]	5391	6800[e]	6872	4455[e]	4237
1200	3151[f]	3034	5492[f]	5457	4496[f]	4681	5947[d]	6083				
1500	3612[f]	3498	6264[f]	6264	5109[f]	5380	6778[d]	6983				

[a] H. L. Johnston and K. E. McCloskey, J. Phys. Chem. **44**, 1038 (1939).
[b] J. A. Bearden, Phys. Rev. **56**, 1023 (1939).
[c] H. L. Johnston and E. R. Grilly, J. Phys. Chem. **46**, 948 (1942).
[d] V. Vasilesco, Ann. Phys. (Paris), Sér. 11, **20**, 292 (1945).
[e] M. Trautz and R. Zink, Ann. der Physik **7**, 427 (1930).
[f] E. Rammler and K. Breitling, Die Wärme (Z. für Dampfkessel u. Maschinenbetrieb) **60**, 620 (1937).

defined collisions and contribute to the transport properties.

Let the Cartesian coordinates of two colliding molecules, A and B (of mass m_A and m_B), be expressed in terms of the Cartesian coordinates of the center of mass, C, and the variables r and θ (see Fig. 1); thus:

$$
\begin{aligned}
x_A &= x_C + [m_B/(m_A+m_B)]r\cos\theta, \\
y_A &= y_C + [m_B/(m_A+m_B)]r\sin\theta, \\
z_A &= z_C, \\
x_B &= x_C - [m_A/(m_A+m_B)]r\cos\theta, \\
y_B &= y_C - [m_A/(m_A+m_B)]r\sin\theta, \\
z_B &= z_C.
\end{aligned}
\tag{18}
$$

The kinetic energy is then given by the sum of two terms, one referring to the motion of the center of mass and the other to the motion relative to the center of mass:

$$T = T_C + \tfrac{1}{2}\mu[\dot{r}^2 + r^2\dot{\theta}^2]. \tag{19}$$

From Eqs. (1) and (19), the Lagrangian for the motion may then be obtained, and from it the equations of motion:

$$r^2\dot{\theta} = bg. \tag{20}$$

$$\tfrac{1}{2}\mu\dot{r}^2 + \tfrac{1}{2}\mu\left[\frac{b^2g^2}{r^2}\right] + E(r) = \tfrac{1}{2}\mu g^2, \tag{21}$$

in which $b=$ the distance of closest approach if $E(r)$ were zero so that the molecules would not be deflected, and $g=$ initial velocity with which the molecules approach one another, while they are still far apart. At this point it is convenient to introduce the following reduced variables:

$$R = r/r_o, \tag{22}$$

$$\beta = b/r_o, \tag{23}$$

$$K = \tfrac{1}{2}\mu g^2/\epsilon, \tag{24}$$

$$V = (K\beta^2/R^2) - (4/R^6) + (4/R^{12}). \tag{25}$$

Then Eq. (21) becomes:

$$K = \tfrac{1}{2}[\mu r_o^2/\epsilon]\dot{R}^2 + V. \tag{26}$$

This represents the one-dimensional motion (with respect to R) of a particle of mass $[\mu r_o^2/\epsilon]$ and total energy K moving in a potential field, V; the latter potential field is defined in Eq. (25).

Figure 2 shows the shape of the V-curves for several values of $K\beta^2$; the hump in the effective potential is due to the term $K\beta^2/R^2$, which is called the centrifugal potential. It is not difficult to show that there exists a critical value of $K\beta^2$:

$$[K\beta^2]_c = (36/25)(5)^{\frac{1}{3}} = 2.4624, \tag{27}$$

above which there are no humps in the effective potential curves; from this, it may be shown that when K is greater than $\tfrac{4}{5}$ the system can pass over the hump for all values of β.

For values of K less than $\tfrac{4}{5}$, there is a critical value of beta, β_o; when β is larger than β_o, the system does not have enough energy to get over the hump, and consequently the molecules are not able to get very close together; when β is

less than β_o, on the other hand, the system passes over the hump and the molecules are permitted to come close together. In the latter case, if K is just slightly larger than the value of V at the hump, the two molecules will spend a considerable time at a separation, R, corresponding to the hump; meanwhile they are rotating with an angular velocity given by Eq. (20). Hence, for such collisions the molecules "orbit" for an indefinite number of revolutions before flying apart.

B. Development of Formula for Angle of Deflection

The only feature of a collision which affects the transport properties is the angle of deflection of the trajectory

$$\chi = \pi - 2\theta_m. \tag{28}$$

Here θ_m, as may be seen from Fig. 1, is the value of θ at the point of closest approach. To determine the trajectory, it is necessary to obtain an expression for θ_m which is independent of time. If we let

$$y = 1/R = r_o/r, \tag{29}$$

then

$$dy/d\theta = -\dot{R}/R^2\dot{\theta}. \tag{30}$$

On substituting for $\dot{R}$ and $\partial^2\theta/\partial t^2$ from Eqs. (26) and (20), and for $b = \beta r_o$

$$dy/d\theta = -(1/\beta)[1 - (V/K)]^{\frac{1}{2}}, \tag{31}$$

TABLE VI. Tabulation and comparison of force constants from viscosity data and 2nd virial coefficients.

	Constants determined from viscosity data (See Table V)			Constants determined from 2nd virial coefficient		
Gas	ϵ/k	r_0	Ref.	ϵ/k	r_0	Ref.
Air	97.0	3.617	a			
H_2	33.3	2.968	a	37.02	2.92	c,d
N_2	91.46	3.681	a	95.9	3.72	e
CO_2	190	3.996	a	185	4.57	f
N_2O	220	3.879	a	189	4.59	f
NO	119	3.470	a	131	3.17	f
CH_4	136.5	3.822	a	142.7	3.81	f
O_2	113.2	3.433	a	117.5	3.58	e
CO	110.3	3.590	a	95.33	3.65	d
A	124.0	3.418	b	119.5	3.41	g
Ne	35.7	2.80	b	35.7	2.74	g
He	6.03	2.70	b	6.03	2.63	g

a H. L. Johnston, and K. E. McCloskey, J. Phys. Chem. **44**, 1038 (1939).
b H. L. Johnston and E. R. Grilly, J. Phys. Chem. **46**, 948 (1942).
c J. DeBoer and A. Michels, Physica **5**, 945 (1938); **6**, 97 (1939).
d J. Corner, Proc. Roy. Soc. **58**, 737 (1946).
e J. O. Hirschfelder and W. E. Roseveare, J. Phys. Chem. **43**, 15 (1939).
f J. O. Hirschfelder, F. T. McClure, C. F. Curtiss, and D. W. Osborne, NDRC-A 116.
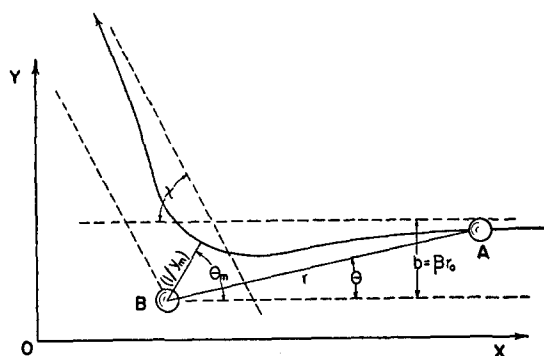g R. A. Buckingham, Proc. Roy. Soc. **A168**, 264 (1938).

FIG. 1a. Pictorial representation of a normal molecular encounter.
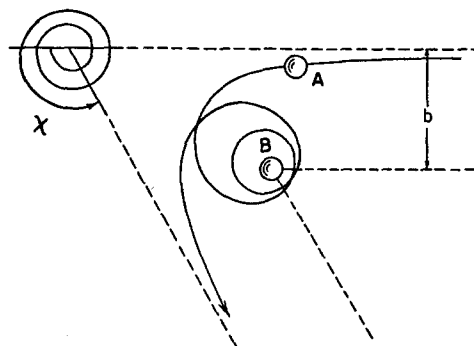

FIG. 1b. The molecular encounter typical of certain low energy collisions in which orbiting takes place at distances of a few angstroms and the molecules separate of their own accord. Such collisions occur when K is less than 0.8 and β is in the vicinity of β_0.

and integrating,

$$\chi = \pi - 2\beta$$

$$\times \int_0^{y_m} dy/[1 - \beta^2 y^2 + (4/K)(y^6 - y^{12})]^{\frac{1}{2}}, \quad (32)$$

where y_m is the lowest root for which the denominator of the integrand vanishes.

To facilitate the numerical integration, y was replaced by uy_m and the integral rearranged into the form

$$\chi = \pi - \frac{2\beta y_m}{a} \int_0^1 du/t[1 + (4/Ka^2)f(t^2)]^{\frac{1}{2}}, \quad (33)$$

where

$$t = (1 - u^2)^{\frac{1}{2}}, \quad (34)$$

$$a^2 = 1 - (8/K)y_m^6 + (20/K)y_m^{12}, \quad (35)$$

$$\beta^2 y_m^2 = 1 + (4/K)y_m^6 - (4/K)y_m^{12}, \quad (36)$$

$$f(t^2) = y_m^6[3t^2 - t^4] \\ + y_m^{12}[1 - 6t^2 - (1 - t^2)^6](1/t^2). \quad (37)$$

When $t = 0$, $f(t^2)$ and $df(t^2)/d(t^2)$ are both zero. The value of $[1 + (4/Ka^2)f(t^2)]$ varies smoothly as t^2 goes from one, when $u = 0$, to zero, when $u = 1$.

We can approximate the function

$$F(t^2) = 1/[1 - (4/Ka^2)f(t^2)]^{\frac{1}{2}} \quad (38)$$

by the polynomial:

$$F(t^2) = 1 + At^2 + Bt^4 + Ct^6 + Dt^8, \quad (39)$$

evaluating $F(t^2)$ at $t^2 = 0$, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, and 1 to determine the constants. With this transformation of the integrand, it is now easy to evaluate χ.

$$\chi = \pi - (2\beta y_m/a) \int_0^1 [F(t^2)/t]du, \quad (40)$$

$$\chi = \pi - 2\beta y_m/a[k_{-1} + Ak_1 + Bk_3 + Ck_5 + Dk_7], \quad (41)$$

in which

$$k_n = \int_0^1 t^n du = (\pi/2)\left[\frac{(n+1)!}{2^{n+1}\left[\left(\frac{n+1}{2}\right)!\right]^2}\right]. \quad (42)$$

To consolidate this formula for computing, we introduce the new parameters c and z defined by the relations:

$$c = (2/K)[1 + (1 + K)^{\frac{1}{2}}], \quad (43)$$

$$cz = (4/K)y_m^6, \quad \text{or} \quad (c+1)z^2 = (4/K)y_m^{12}. \quad (44)$$

Then

$$\chi = \pi - (\pi/6)[1 + cz - (c+1)z^2]^{\frac{1}{2}} \\ \times \{1 + 1/[1 - 2cz + 5(c+1)z^2]^{\frac{1}{2}} \\ + 2/[1 - (21/16)cz \\ + (2343/1024)(c+1)z^2]^{\frac{1}{2}} \\ + 2/[1 - (5/16)cz \\ + (341/1024)(c+1)z^2]^{\frac{1}{2}}\}. \quad (45)$$

Equation (45) is not sufficiently accurate for $0.1 \leq K \leq 0.8$. However, a closer approximation may be had for χ in the vicinity of orbiting by requiring that the curve fit include $F(t_1^2)$, where t_1^2 is defined as the value of t^2 for which

$$[1 + (4/Ka^2)f(t^2)]^{\frac{1}{2}} = 0 \quad (46)$$

or

$$t_1^2 = 1 - [z/z_o]^{\frac{1}{2}} = 1 - u_1^2. \quad (47)$$

The result of this integration is an elaboration of the previous equation:

$$\chi = \pi - Y_1[Z_1 + Y_2 Z_2 + Y_3(Z_3 + Z_3')$$
$$+ Y_4 Z_4 + Y_5 Z_5 + Y_6 Z_6],$$

in which

$Y_1 = 2[1 + cz - (c+1)z^2]^{\frac{1}{2}}$,

$Y_2 = [t_1^2 - \frac{3}{4}]^{-1}[1 - (5/16)cz$
$\qquad\qquad + (341/1024)(c+1)z^2]^{-\frac{1}{2}}$,

$Y_3 = \{1 + [3t_1^2 - 2 - t_1^4]cz + [5 + (1/t_1^2)(1 - 6t_1^2$
$\qquad\qquad - (1 - t_1^2)^6)](c+1)z^2\}^{-\frac{1}{2}}$,

$Y_4 = [\frac{1}{2} - t_1^2]^{-1}[1 - \frac{3}{4}cz + (31/32)(c+1)z^2]^{-\frac{1}{2}}$,

$Y_5 = [t_1^2 - \frac{1}{4}]^{-1}[1 - (21/16)cz$
$\qquad\qquad + (2343/1024)(c+1)z^2]^{-\frac{1}{2}}$,

$Y_6 = t_1^{-2}[1 - 2cz + 5(c+1)z^2]^{-\frac{1}{2}}$,

$Z_1 = 4[1 - t_1^2]^{-1}[h_3 - (\frac{3}{4} + t_1^2)h_1 + \frac{3}{4}t_1^2 h_{-1}]$, \qquad (48)

$Z_2 = 4[h_3 - (1 + t_1^2)h_1 + t_1^2 h_{-1}]$,

$Z_3 = [(t_1^2 - 1)(t_1^2 - \frac{3}{4})]^{-1}[h_3 - (7/4)h_1 + \frac{3}{4}h_{-1}]$,

$Z_3' = [t_1^2(t_1^2 - \frac{1}{4})(t_1^2 - \frac{1}{2})]^{-1}[(5\pi/32) - h_5$
$\qquad - \frac{3}{4}((3\pi/16) - h_3) + \frac{1}{8}((\pi/4) - h_1)]$,

$Z_4 = 8[((5\pi/32) - h_5) - (\frac{1}{4} + t_1^2)((3\pi/16) - h_3)$
$\qquad\qquad + \frac{1}{4}t_1^2((\pi/4) - h_1)]$,

$Z_5 = 16[((5\pi/32) - h_5) - (\frac{1}{2} + t_1^2)((3\pi/16) - h_3)$
$\qquad\qquad + \frac{1}{2}t_1^2((\pi/4) - h_1)]$,

$Z_6 = 8[(\frac{3}{4} + t_1^2)((3\pi/16) - h_3)$
$\qquad - ((5\pi/32) - h_5) - (\frac{1}{8} + \frac{3}{4}t_1^2)((\pi/4) - h_1)$
$\qquad\qquad + \frac{1}{8}t_1^2((\pi/2) - h_{-1})]$,

and where

$$h_n(u_1) = \int_0^{u_1} (1 - u^2)^{n/2} du.$$

For values of K greater than 0.8 there is no physical basis for using t_1, and the function is satisfactorily represented by either equation, as was shown by the fact that both formulas gave the same results for $K = 1$ and $K = 100$, letting $t_1^2 = 0.6$ in the modified form.

For small values of z, it is convenient to express χ in the series:

$$\chi = -0.9375\pi cz - 0.5713\pi c^2 z^2$$
$$+ 1.3535(c+1)z^2. \quad (49)$$

This was obtained by expanding

$$[1 + (4/Ka^2)f(t^2)]^{-\frac{1}{2}}$$

TABLE VII. Conditions for orbiting.

K	β_0	z_0	z_1
0.1	2.5367	0.01261	0.8299
0.2	2.2549	0.02557	0.7260
0.4	1.9988	0.05366	0.5566
0.6	1.8567	0.08830	0.4030
0.8	1.7544	0.17082	0.17082

into powers of z and integrating directly the resulting polynomial in t^n.

Values of the angle of deviation χ have been tabulated,[**] along with the values of K, z, and β. The value of β corresponding to each value of z can be determined from the relation

$$\beta = [2/[1 + (1+K)^{\frac{1}{2}}]]^{1/6}$$
$$\times z^{-1/6}[1 + cz - (c+1)z^2]^{\frac{1}{2}}, \quad (50)$$

from which it is clear that z goes from zero (corresponding to β infinite) to unity (corresponding to β zero). As long as K is equal to, or greater than 0.8, there is a one-to-one correspondence between values of z and values of β. When K is equal to or less than 0.8, there are additional complications corresponding to orbiting for critical values of β. The orbiting occurs
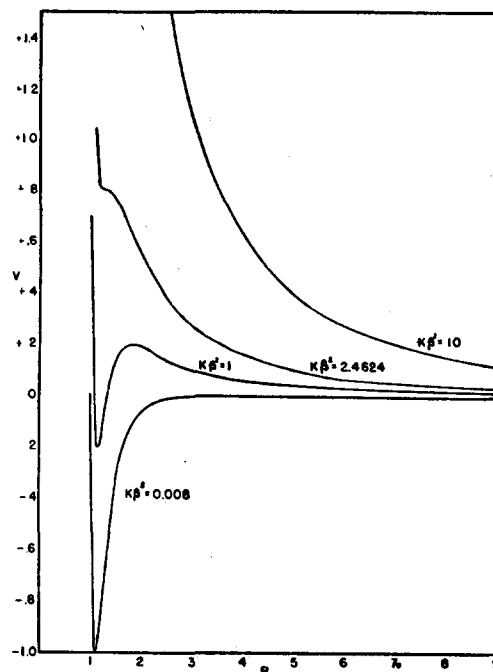

FIG. 2. Effective potential curves for several values of $K\beta^2$. The combination of the original potential and the centrifugal energy leads to effective potential energy curves exhibiting humps when $K\beta^2$ is less than the critical value, 2.4624. No orbiting is possible for collisions in which K is greater than 0.8.

when

$$[d^2\theta/dy^2]_{ym}=0. \qquad (51)$$

This can be expressed by the requirement that $a=0$ [note Eq. (22)], or, letting the subscript "o" indicate orbiting:

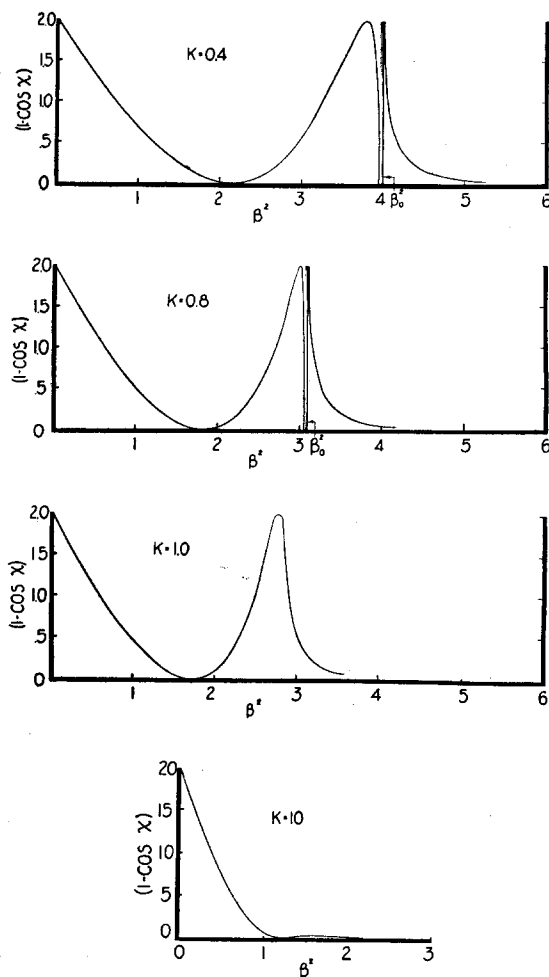$$z_o=\frac{2}{5}\left[\frac{1-(1-(5/4)K)^{\frac{1}{2}}}{1+(1+K)^{\frac{1}{2}}}\right]. \qquad (52)$$

FIG. 3. $(1-\cos\chi)$ *versus* β^2 for several values of K. For small values of K, corresponding to low energy collisions, the molecules "orbit" around each other when β^2 is close to the critical value, β_o^2. In this region, $1-\cos\chi$ oscillates rapidly between the values zero and two. This orbiting no longer takes place when K is greater than 0.8. The collision cross section, $S^{(1)}(K)$, is the integral of $(1-\cos\chi)$ with respect to β^2. The contribution to this integral from collisions in which β^2 is less than 2 is due to the repulsive component of the intermolecular potential. The contribution due to collisions in which β^2 is greater than 2 is due to the energy of attraction; this area disappears for high energy collisions as, for example, in the case $K=10$.

TABLE VIII. Collision cross sections.

K	$S^1(K)$	$S^2(K)$	$S^4(K)$
0.1	5.445	6.107	6.57
0.2	4.476	4.800	5.16
0.4	3.368	3.846	4.17
0.6	2.909	3.347	3.601
0.8	2.523	3.082	3.312
0.9	2.505	2.933	3.183
0.95	2.467	2.840	3.055
1.0	2.401	2.798	2.988
1.2	2.1007	2.7392	2.9186
1.4	1.8714	2.6399	2.7741
1.6	1.6974	2.4722	2.6244
1.8	1.5656	2.2958	2.4858
2.0	1.4801	2.1513	2.3582
2.5	1.2938	1.8240	2.0644
3.0	1.1890	1.6173	1.8382
4.0	1.0673	1.3755	1.5415
5.0	0.9981	1.2439	1.3697
10.0	0.8558	1.0113	1.0664
15.0	0.7974	0.9345	0.9749
20.0	0.7612	0.8910	0.9263
50.0	0.6610	0.7784	0.8085
100.0	0.5936	0.7036	0.7326

For each value of z_o there is a critical value of beta, β_o; these are given for the various values of K in Table VII. As z approaches z_o, χ becomes infinite. This behavior is correctly represented by the approximate expression for χ, [Eq. (45)]. Here the term $[1-2cz+5(c+1)z^2]^{-\frac{1}{2}}$ approaches infinity. When $K=0.8$, there is a critical value of β for which orbiting occurs, but there is still a one-to-one correspondence between z and β. For collisions where the energy K is less than 0.8 between $z=z_o$ and $z=z_1$, there are two values which when substituted into Eq. (50) give the same value of β. It is convenient to define z_1 as the second value of z for which $\beta=\beta_o$, and its numerical value is also given in Table VII.

Physically there is no significance to values of z lying between z_o and z_1. If β is just barely larger than β_o, the molecules after orbiting at a separation corresponding to z must separate because they do not have quite enough energy to get over the energy hump. The value of χ at z_1 should be infinite. Although it becomes very large according to the approximate formula, Eq. (45), it does not actually become infinite unless one of the values of $t^2=\frac{1}{4}, \frac{1}{2}$, or $\frac{3}{4}$, should accidentally correspond to the separation of the energy hump. However, this does not lead to any serious error in the next integration to obtain the reduced cross section, $S^{(1)}(K)$.

TABLE IX. Tabulation of the constants for the equations of $S^{(l)}(K)$.

$$S(K)^{(l)} = \sum_i A_i^{(l)} K^{n_i^{(l)}} e^{-a_i^{(l)}K}$$

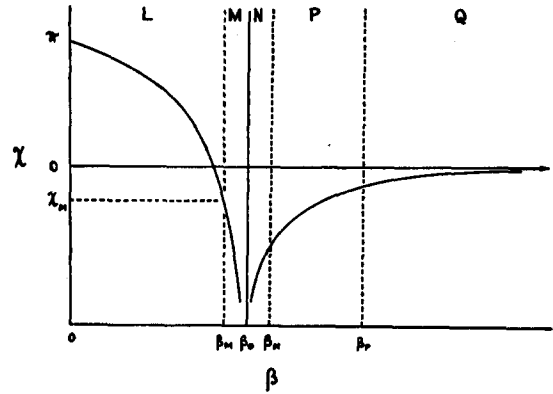| i	$A_i^{(1)}$	$n_i^{(1)}$	$a_i^{(1)}$
1	$+1.2120$	-0.155	0
2	$+1.0782$	-0.5	0.439
3	$+19.49$	$+2.126$	3.675
4	-4.255×10^{81}	$+154$	194
5	-1.677×10^{16}	$+23.4$	45
6	$+1.705 \times 10^{5}$	$+4.425$	29.1
i	$A_i^{(2)}$	$n_i^{(2)}$	$a_i^{(2)}$
1	$+1.3719$	-0.145	0
2	$+1.1812$	-0.789	0.190
3	$+2.724$	-0.697	0.67742
4	-8.9976×10^{2}	$+3.01$	6.7461
5	$+3.162 \times 10^{66}$	$+118.6$	132.2
6	$+9.3325 \times 10^{188}$	$+363.5$	443.25
7	$+8.4723 \times 10^{54}$	$+82.51$	140.42
8	-5.0315×10^{6}	$+3.958$	35.989
i	$A_i^{(4)}$	$n_i^{(4)}$	$a_i^{(4)}$
1	$+1.3959$	-0.140	0
2	$+0.5722$	-0.5	0.1350
3	$+2.9001$	-0.41085	0.49593
4	-7.1895×10^{2}	$+7.300$	7.5377
5	-3.19×10^{29}	$+66.103$	69.1675
6	-7.9433×10^{366}	$+771.9$	851.73
7	-1.3975×10^{3}	$+1.809$	16.282
8	-1.1067×10^{31}	$+37.162$	92.906
9	-8.6147×10^{47}	$+73.074$	121.79
10	-4.3055×10^{362}	$+683.53$	854.41

FIG. 4. Schematic diagram of χ versus β, showing the zones used in the evaluation of the collision cross sections for low energy collisions.

C. Evaluation of the Reduced Collision Cross-Section Integrals

Once the angles of deflection, χ, have been determined for individual collisions, the task of evaluating the reduced collision cross sections presents itself. The integrals $S^{(l)}(K)$ were defined in Eq. (2).

When K is greater than 0.8 the integral is easily evaluated by changing the integration variable from β to z and writing $S^{(l)}(K)$ in the form:

$$S^{(l)}(K) = \frac{\left[\frac{2}{3}(4/cK)^{\frac{1}{2}} \right]}{\left[2 - \frac{[1+(-1)^l]}{[l+1]} \right]}$$
$$\times \int_0^1 (1-\cos^l \chi) \frac{[1-2cz+(c+1)z^2]}{z^{4/3}} dz. \quad (53)$$

This can be integrated numerically by using the χ values described in the previous section. The curves of $(1-\cos\chi)$ versus β^2 are shown in Fig. 3.

On the other hand, when K is less than 0.8, the curve of χ versus β is discontinuous at β_o, as is shown in Fig. 4. Accordingly, it is convenient to break up the integral in Eq. (2) into five integrals, as is indicated in the figure, thus:

$$S^{(l)}(K) = L^{(l)}(K) + M^{(l)}(K)$$
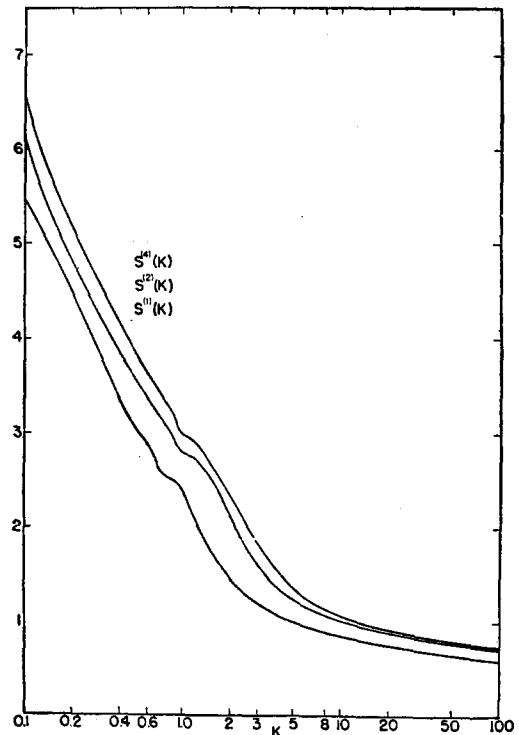$$+ N^{(l)}(K) + P^{(l)}(K) + Q^{(l)}(K). \quad (54)$$

FIG. 5. The reduced collision cross sections, $S^{(l)}(K)$. The function $S^{(1)}(K)$ is used to determine diffusion coefficients. It is considerably smaller than the cross section $S^{(2)}(K)$, used for heat conductivity and viscosity. $S^{(4)}(K)$ is used for third-order corrections. The indentation for K between 0.8 and 1.0 is due to the orbiting. The irregular wavy pattern of the cross sections for small values of K is real and not due to computational errors. The cross sections for very low velocity collisions should be corrected for quantum-mechanical effects.

The integrals $L^{(l)}(K)$ and $P^{(l)}(K)$ are obtained by using numerical integration in the form given in Eq. (53) with the appropriate limits. The integrals $M^{(l)}(K)$ and $N^{(l)}(K)$ are evaluated by curve-fitting χ versus β with an equation of the form

$$\chi^2 = a'/(\beta^2 - \beta_o^2), \quad \text{where} \quad a' = \text{a constant,} \quad (55)$$

and integrating Eq. (2) analytically between the proper limits. The integrals $Q^{(l)}(K)$, which extend from $\beta = \beta_P$ to $\beta = \infty$ (or $z = z_P$ to $z = 0$), are calculated by making use of Eq. (49), which gives χ for small values of z; the latter is substituted into Eq. (53) and $(1 - \cos^l\chi)$ is expanded, the integration then being executed analytically.

The equations obtained for the $Q^{(l)}(K)$ and the $M^{(l)}(K)$ are:

$$Q^{(1)}(K) = \tfrac{1}{3}[4/cz_PK]^{\frac{1}{3}}[2.6024(cz_P)^2$$
$$-1.2707(cz_P)^3 - 3.2991(cz_P)^4$$
$$+0.65345(cz_P)^5],$$
$$Q^{(2)}(K) = \tfrac{1}{2}[4/cz_PK]^{\frac{1}{3}}[5.2047(cz_P)^2$$
$$-2.5414(cz_P)^3 - 11.7286(cz_P)^4 \quad (56)$$
$$+20.1185(cz_P)^5],$$
$$Q^{(4)}(K) = (5/12)[4/cz_PK]^{\frac{1}{3}}[10.4094(cz_P)^2$$
$$-13.0117(cz_P)^3],$$

$$M^{(1)}(K) = (\beta_o^2 - \beta_M^2)[1 - \cos\chi_M$$
$$+\chi_M \sin\chi_M + \chi_M^2 Ci(-\chi_M)],$$
$$M^{(2)}(K) = \tfrac{3}{4}(\beta_o^2 - \beta_M^2)[1 - \cos2\chi_M$$
$$+2\chi_M \sin2\chi_M - 4\chi_M^2 Ci(-2\chi_M)],$$
$$M^{(4)}(K) = (5/32)(\beta_o^2 - \beta_M^2)[5 - 4\cos2\chi_M \quad (57)$$
$$-\cos4\chi_M + 8\chi_M \sin2\chi_M$$
$$+4\chi_M \sin4\chi_M$$
$$-16\chi_M^2 Ci(-2\chi_M)$$
$$-16\chi_M^2 Ci(-4\chi_M)].$$

The $N^{(l)}(K)$ have the same form as the $M^{(l)}(K)$.

The values of the $S^{(l)}(K)$ obtained by the two procedures outlined above are shown graphically in Fig. 5 and the values are tabulated in Table VIII. These three curves were then fitted with equations of the form

$$S^{(l)}(K) = \sum_i A_i{}^{(l)} K^{n_i(l)} e^{-a_i(l)K}, \quad (58)$$

the constants for the equations appearing in Table IX.

D. Evaluation of $W^{(l)}(n;x)$

To obtain the $W^{(l)}(n;x)$, the expressions for the $S^{(l)}(K)$ of Eq. (58) are substituted into Eq. (3),

TABLE X. Expressions for $W^{(l)}(n;x)$.

$x = \epsilon/kT$

$W^{(1)}(1;x) = \tfrac{1}{4}x^3[2.11114x^{-2.845} + 1.43329(x+0.439)^{-2.5} + 566.494(x+3.675)^{-5.126} - 0.02077 \exp(-0.8093x)$
$\qquad\qquad -0.2159 \exp(-0.5867x) + 0.003726 \exp(-0.2552x)]$

$W^{(1)}(2;x) = \tfrac{1}{4}x^4[6.00619x^{-3.845} + 3.58323(x+0.439)^{-3.5} + 2903.85(x+3.675)^{-6.126} - 0.01681 \exp(-0.8144x)$
$\qquad\qquad -0.01267 \exp(-0.6089x) + 0.0009506 \exp(-0.2895x)]$

$W^{(1)}(3;x) = \tfrac{1}{4}x^5[23.0938x^{-4.845} + 12.5413(x+0.439)^{-4.5} + 17789(x+3.675)^{-7.126} - 0.01369 \exp(-0.8196x)$
$\qquad\qquad +0.0002752 \exp(-0.3239x) - 0.007714 \exp(-0.6311x)]$

$W^{(2)}(2;x) = \tfrac{1}{6}x^4[6.88155x^{-3.855} + 2.89488(x+.190)^{-3.211} + 7.33242(x+.67742)^{-3.303} - 660079(x+6.7461)^{-7.01}$
$\qquad\qquad +0.03950 \exp(-0.9274x) + 0.03732 \exp(-0.8291x)$
$\qquad\qquad\qquad +0.03888 \exp(-0.6161x) - 0.009625 \exp(-0.2211x)]$

$W^{(2)}(3;x) = \tfrac{1}{6}x^5[26.5284x^{-4.855} + 9.29546(x+0.190)^{-4.211} + 24.2190(x+.67742)^{-4.303} - 4627150(x+6.7461)^{-8.01}$
$\qquad\qquad +0.03663 \exp(-0.9349x) + 0.03094 \exp(-0.8314x)$
$\qquad\qquad\qquad +0.02395 \exp(-0.6232x) - 0.002128 \exp(-0.2489x)]$

$W^{(2)}(4;x) = \tfrac{1}{6}x^6[128.795x^{-5.855} + 39.1432(x+0.190)^{-5.211} + 104.214(x+0.67742)^{-5.303} - 37063500(x+6.7461)^{-9.01}$
$\qquad\qquad +0.03425 \exp(-0.9425x) + 0.02573 \exp(-0.8336x)$
$\qquad\qquad\qquad +0.01493 \exp(-0.6303x) - 0.0005298 \exp(-0.2767x)]$

$W^{(2)}(5;x) = \tfrac{1}{6}x^7[754.095x^{-6.855} + 203.975(x+0.190)^{-6.211} + 552.647(x+0.67742)^{-6.303} - 333942000(x+6.7461)^{-10.01}$
$\qquad\qquad +0.03228 \exp(-0.9501x) + 0.02145 \exp(-0.8359x)$
$\qquad\qquad\qquad +0.009408 \exp(-0.6374x) - 0.0001466 \exp(-0.3045x)]$

$W^{(2)}(6;x) = \tfrac{1}{6}x^8[5169.32x^{-7.855} + 1266.89(x+0.190)^{-7.211} + 3483.33(x+0.67742)^{-7.303} - 3342750000(x+6.7461)^{-11.01}$
$\qquad\qquad +0.03067 \exp(-0.9576x) + 0.01793 \exp(-0.8381x)$
$\qquad\qquad\qquad +0.005997 \exp(-0.6446x) - 0.00004463 \exp(-0.3323x)]$

$W^{(4)}(4;x) = \tfrac{1}{8}x^6[132.154x^{-5.86} + 29.9505(x+0.1350)^{-5.5} + 175.386(x+0.49593)^{-5.58915} - 737383000000(x+7.5377)^{-13.3}$
$\qquad\qquad -0.09163 \exp(-1.0424x) - 0.002420 \exp(-0.9133x) - 0.001657 \exp(-0.4796x)$
$\qquad\qquad -0.003243 \exp(-0.4646x) - 0.01629 \exp(-0.6493x) - 0.008924 \exp(-0.8070x)]$

which integrates to complete gamma-functions:

$$W^{(l)}(n;x) = \tfrac{1}{8}[2-[(1+(-1)^l)/(l+1)]]x^{n+2}$$
$$\times \sum_i A_i^{(l)} \frac{\Gamma[n+n_i^{(l)}+2]}{[x+a_i^{(l)}]^{(n+n_i^{(l)}+2)}}. \quad (59)$$

Equations for the most important $W^{(l)}(n;x)$ are stated explicitly in Table X. The exponential terms are obtained by letting terms of the form

$$C/(x+p)^q = Cp^{-q}e^{-q/p}, \quad C = \text{a constant.} \quad (60)$$

The work presented in this report could not have been carried out without the help of a very efficient computing group under the direction of Jean Patterson. These calculations were made by Ruth Shoemaker, Doris Jayne, Mary Sullivan, Theodore Mesmer, Freda Coen, and Florence Cappon.

The Energy of the C−H Bond in the Three Picolines (Methyl Pyridines)

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The pyrolysis of the three picolines was investigated and the rates of the decomposition were compared with the rate of the decomposition of toluene. It was found that the process of the decomposition of the picolines is analogous to that of toluene, i.e., the rate determining step is the splitting of the picoline molecule into H atom and a picolyl radical. Comparison of the decomposition rates of the picolines and of toluene made it possible to calculate the C−H bond energy for these compounds. These were estimated at 75.5 kcal./mole for α-picoline, 76.5 kcal./mole for β-picoline, and 77.5 kcal./mole for γ-picoline. It was concluded therefore that the resonance energy of the picolyl radical approximates within a few kcal. the resonance energy of the benzyl radical.

THE aim of the present work was to investigate how the resonance energy of an aromatic system is changed when one of the CH groups in the ring is replaced by a N atom. Comparison of the energies of the C−H bond (the bond energy is defined here as the dissociation energy of the bond) in the methyl group of the picolines with that of toluene ought to reveal whether there are any significant variations in the resonance energies of the radicals produced by breaking this bond. Such variations would be shown by parallel differences between the rate of pyrolysis of toluene on the one hand and the picolines on the other.

EXPERIMENTAL

The rates of pyrolysis of the three picolines were measured by the method and technique previously used for toluene, the xylenes,[1] and the fluorotoluenes.[2]

[1] M. Szwarc, J. Chem. Phys. **16**, 128 (1948).
[2] M. Szwarc and J. S. Roberts, J. Chem. Phys. **16**, 609 (1948).

MATERIAL USED

The commercial picolines were purified by several distillations using an efficient column. As in previous work,[1,2] the criterion of purity was that the product recovered from any pyrolysis should give the same rate of decomposition on being pyrolysed once more. By this standard, the distilled β-picoline was sufficiently pure. The α- and γ-picolines gave a constant rate of decomposition after the first pyrolysis, and thus all results reported for these compounds refer to material previously pyrolysed at least once.

RESULTS

The results summarized in Tables IA and B and II indicate that the essential features of the mechanism of the decomposition of the picolines were the same as in the previous cases,[1,2] i.e., the rate determining step is the splitting of the picoline molecule into H and a $C_5H_5N \cdot CH_2 \cdot$ radical. The gases produced in the pyrolysis of γ-picoline consist of 70 percent of H_2 and 30