

tions in dielectric strength probably are caused by holes, cracks, or dust particles in the films. In general, films with the highest dielectric strength were made from baths of higher pH.

6. Skeletonized films have electrical properties in agreement with the concept of their physical structure.

SCHENECTADY, N. Y.

RECEIVED FEBRUARY 16, 1939

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 695]

The Thermodynamic Constants of Bromine Chloride. The Equilibrium Reaction between Nitric Oxide, Bromine, Chlorine, Nitrosyl Bromide and Chloride, and Bromine Chloride

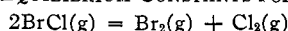
BY CARROL M. BEESON AND DON M. YOST

Introduction

The degree of dissociation of gaseous bromine chloride, BrCl, at room temperature has been determined by several investigators by light absorption methods, and the results are in fair agreement. The use of chemical methods for studying the equilibrium has so far been restricted to studies at rather high temperatures, namely, 500 and 800°. In these determinations mixtures of fused chlorides and bromides, for example the silver chloride-silver bromide pair, are in equilibrium with

The results of all former measurements of the equilibrium constant of reaction (1) are summarized in Table I. The weighted mean value of K at room temperature was obtained by giving to each value a weight inversely proportional to the stated error; the two widely different values of Jost were omitted in calculating the mean. This method of estimating the mean is not free from criticism, but it appears to be as satisfactory as any in arriving at a value that is representative of those obtained by all investigators.

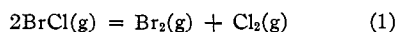
TABLE I
SUMMARY OF EQUILIBRIUM CONSTANTS FOR THE REACTION



$$K_{\text{BrCl}} = P_{\text{Br}_2}P_{\text{Cl}_2}/P_{\text{BrCl}}^2$$

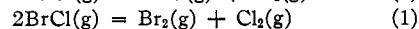
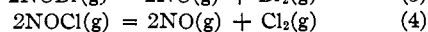
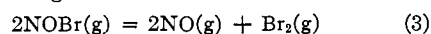
Date	Authors	Method	Temp., °C.	K
1930	Gray and Style ¹	Light absorption	Room	0.132 to 0.125
1931	Jost ²	Light absorption	Room	.10 to .22
1933	Dickinson and Murdock ³	Light absorption	Room	.12 ± 0.01
1934	Vesper and Rollefson ⁴	Light absorption	28	.107 ± .002
1935	Braner and Victor ⁵	Light absorption	Room	.144 ± .003
1935	Jellinek and Schütza ⁶	KCl(l), KBr(l), Br ₂ (g), Cl ₂ (g), BrCl(g), and other salt pairs	800	.12
1938	Schütza ⁷	AgCl(l), AgBr(l), Br ₂ (g), Cl ₂ (g), BrCl(g), also PbCl ₂ , PbBr ₂ , and other salt pairs	500	.1325
			800	.140
		Weighted mean value at room temperature		.126

gaseous chlorine, bromine, and bromine chloride. A knowledge of the activities of the component salts is necessary in order to evaluate the partial pressures of the three gases. The reversible gas reaction under consideration is



$$K_{\text{BrCl}} = \frac{P_{\text{Br}_2}P_{\text{Cl}_2}}{P_{\text{BrCl}}^2} \quad (2)$$

In the present paper are described the results of equilibrium measurements on the gaseous system nitric oxide, bromine, chlorine, nitrosyl bromide and chloride, and bromine chloride in the temperature range from 372 to 492°K. The reversible reactions taking place may be regarded as the following



and measurements of the total pressure of the system together with a knowledge of its composition make possible the calculation of K_{BrCl} .

- (1) Gray and Style, *Proc. Roy. Soc. (London)*, **A123**, 582 (1929).
 (2) Jost, *Z. physik. Chem.*, **A153**, 143 (1931).
 (3) Dickinson and Murdock, private communication.
 (4) Vesper and Rollefson, *THIS JOURNAL*, **56**, 620 (1934).
 (5) Brauer and Victor, *Z. Elektrochem.*, **41**, 508 (1935).
 (6) Jellinek and Schütza, *Z. anorg. Chem.*, **227**, 52 (1936).
 (7) Schütza, *ibid.*, **239**, 245 (1938).

The equilibrium constants for reaction (3) were determined by Blair, Brass and Yost,⁸ and are given, as a function of the temperature, by the expression

$$K_{\text{NOBr}} = \frac{P_{\text{NO}}^2 P_{\text{Br}_2}}{P_{\text{NOBr}}^2} \quad (5)$$

$$\log_{10} K_{\text{NOBr}}(\text{cm.}) = -9.325 - (1919/T) + 6.750 \log_{10} T - 0.00407T + 1.27 \times 10^{-6}T^2 \quad (6)$$

The constants for reaction (4) were determined recently by Beeson and Yost⁹ and may be calculated from the relation

$$K_{\text{NOCl}} = \frac{P_{\text{NO}}^2 P_{\text{Cl}_2}}{P_{\text{NOCl}}^2} \quad (7)$$

$$\log_{10} K_{\text{NOCl}}(\text{cm.}) = -2.808 - (3591.0/T) + 4.1457 \log_{10} T - 0.0023406T + 0.52915 \times 10^{-6}T^2 \quad (8)$$

In both cases the $K(\text{cm.})$ are expressed in centimeters of mercury at 0° and sea level, and they have been corrected for gas imperfections. The experimental errors amount to $\pm 2\%$ for K_{NOBr} and from ± 1 to $\pm 2\%$ for K_{NOCl} .

Preparation of Materials and Experimental Methods

Materials.—The nitric oxide and chlorine were prepared with great care and were portions of the same materials used in the investigation of nitrosyl chloride.⁹ The chlorine contained less than 0.1% of hydrogen chloride, and the nitric oxide was of high purity and free from other oxides of nitrogen.

Bromine was prepared by treating a saturated solution of twice recrystallized potassium bromate and bromide with chemically pure sulfuric acid. The bromine was distilled from this mixture and then dried over, and repeatedly distilled from, specially purified anhydrous calcium bromide, fresh portions of the latter being used for each distillation. Only the middle fraction of the bromine was used in the equilibrium measurements. Both the bromine and chlorine were condensed and sealed in glass capsules equipped with easily breakable tips.

Experimental Procedure.—The nitric oxide, bromine, and chlorine were introduced into a one-liter evacuated Pyrex glass flask, the manner of filling differing but little from that described in the papers on nitrosyl chloride and bromide.^{8,9} At no time did the chlorine and bromine come in contact with stopcock grease or other organic matter; glass enclosed magnetic devices were used to break the capsules containing these substances, and the pressures were measured by means of a glass click gage. The thermostated mercury manometer had an inside diameter of 2.15 cm., and the heights of its arms were read to 0.005 cm. with a cathetometer whose scale had been calibrated against a standard decimeter, ruled on glass, from the National Bureau of Standards. The reaction flask was immersed in a hydrogenated cottonseed oil filled thermostat whose temperature was kept constant to $\pm 0.1^\circ$. Temperatures were measured to 0.05° with mercury thermometers which were calibrated periodically against thermometers from the National Bureau of Standards.

Corrections.—Corrections were made to take account of (1) the thermal expansion of the Pyrex glass reaction ves-

sel,¹⁰ (2) the exposed part of the thermometer, (3) the height of the menisci and temperature of the mercury in the manometer,¹¹ (4) the acceleration due to gravity (at Pasadena $g = 979.57 \text{ cm./sec.}^2$; the standard is $g = 980.67 \text{ cm./sec.}^2$), (5) the obnoxious volume, and (6) gas imperfections. Other minor corrections were made to take account of the small temperature changes in the air filled side of the manometer and the small amount of nitric oxide present in a side-arm when it was sealed off.

The most important single correction involving the nature of the reaction vessel was that due to the small obnoxious volume (dead space) of the click gage and its connecting tube. This correction was made on the assumption that equilibrium was established in the dead space corresponding to its temperature, namely, that of the room.

Corrections were made for the effect of gas imperfections in the manner described below. The principal effect of these corrections is on the magnitudes of those partial pressures which are small. This is because small partial pressures are obtained as differences in larger pressures, and if the gases present at the larger pressures are imperfect, the differences in their pressures can be in considerable error if corrections are not made.

Results of the Equilibrium Measurements

In order to calculate the equilibrium constants for the dissociation of bromine chloride, the following independent relations were derived from the perfect gas laws

$$K_1 = \frac{P_{\text{NO}}^2 P_{\text{Cl}_2}}{P_{\text{NOCl}}^2}$$

$$K_2 = \frac{P_{\text{NO}}^2 P_{\text{Br}_2}}{P_{\text{NOBr}}^2}$$

$$K_{\text{BrCl}} = \frac{P_{\text{Br}_2} P_{\text{Cl}_2}}{P_{\text{BrCl}}^2}$$

$$P_{\text{NO}} = P_{\text{NO}}^0 - P_{\text{NOCl}} - P_{\text{NOBr}} = P_{\text{NO}}^0 - 2\Delta P$$

$$P_{\text{Cl}_2} = P_{\text{Cl}_2}^0 - \frac{1}{2}P_{\text{NOCl}} - \frac{1}{2}P_{\text{BrCl}}$$

$$P_{\text{Br}_2} = P_{\text{Br}_2}^0 - \frac{1}{2}P_{\text{NOBr}} - \frac{1}{2}P_{\text{BrCl}}$$

where P_{NO}^0 , $P_{\text{Cl}_2}^0$ and $P_{\text{Br}_2}^0$ are the partial pressures that would obtain if no reaction took place, the other P_s are actual partial pressures, and ΔP is the difference between the observed pressure, P , and the pressure calculated on the assumption of no reaction, $\Delta P = P_{\text{NO}}^0 + P_{\text{Cl}_2}^0 + P_{\text{Br}_2}^0 - P$. These equations, when solved under the assumption that K_1 is small (about 0.1%) compared to K_2 , yield

$$P_{\text{NOBr}} = \left[K_2 (P_{\text{Br}_2}^0 + \Delta P - P_{\text{Cl}_2}^0) + \frac{P_{\text{NO}}^2}{4} + 4K_1 K_2 \frac{\Delta P^2}{P_{\text{NO}}^2} \right]^{1/2} \frac{P_{\text{NO}}}{K_2} - P_{\text{NO}}^2 / 2K_2$$

$$P_{\text{NOCl}} = 2\Delta P - P_{\text{NOBr}}$$

$$P_{\text{BrCl}} = P - P_{\text{NO}} - P_{\text{NOBr}} - P_{\text{NOCl}} - P_{\text{Cl}_2} - P_{\text{Br}_2}$$

and these, together with the other more obvious relations, permit the calculation of K_{BrCl} . The value used for the gas constant R was 6236.6

(8) Blair, Brass and Yost, *THIS JOURNAL*, **56**, 1916 (1934).

(9) Beeson and Yost, *J. Chem. Phys.*, **7**, 44 (1939).

(10) "International Critical Tables," Vol. 11, 1929, p. 93.

(11) *Ibid.*, Vol. I, 1929, p. 73.

ml. cm./deg. mole and it was calculated from the "International Critical Tables" value of 82.06 ml. atm./deg. mole.¹²

It was soon found that equilibrium was established rapidly at all temperatures investigated. This fact is of interest in view of the fact that nitric oxide reacts slowly with chlorine or bromine alone; evidently the reaction mechanism in the mixture involves rapid reactions not possible when only one halogen is present with nitric oxide. This same phenomenon was observed by McMorris and Yost¹³ in the investigation of gaseous mixtures of nitric oxide, chlorine, iodine, and iodine monochloride.

Three separate fillings of the reaction vessel were made with the varying initial amounts of reactants shown in Table II. In Table III are presented the equilibrium pressures P for the three fillings together with the values of the equilibrium constants $K = P_{\text{Br}_2} P_{\text{Cl}_2} / P_{\text{BrCl}}^2$. The constants K' were calculated without taking into account gas imperfections; the constants K were obtained after correcting for the imperfections. All pressures are expressed in international centimeters of mercury at 0°.

It was found not difficult to adjust the temperature of the thermostat to a predetermined value, and this made it possible to determine equilibrium pressures at the same temperature for all runs. Measurements were made both while ascending and descending the temperature scale, and the two final values of P , for any temperature, obtained by approaching equilibrium from the two directions, did not differ by more than 0.02 cm.

TABLE II
INITIAL AMOUNTS OF REACTANTS

Volume of reaction vessel = 1049.7 ml. at 20°. Volume of dead space = 2.3 ml. at 20°.

Run	Br ₂ , g.	Cl ₂ , g.	Nitric oxide		Vol., ml. ^a	Br ₂	Approx. mol. Ratios	
			Press. Int. cm. Hg at 0°	Temp., °C.			Cl ₂	NO
I	0.7491	0.6544	24.18	23.97	1088.2	1	2.0	3.0
11	.7737	.7487	25.01	22.25	1088.4	1	2.2	3.1
111	.9938	.5358	27.26	22.20	1088.9	1	1.2	2.6

^a This is volume of NO before it was condensed and the side-arm of the vessel sealed off.

Discussion

The values of K' listed in Table III were calculated under the assumption that all gases obeyed the perfect gas laws. A comparison of the K'

(12) "International Critical Tables," Vol. 1, 1929, p. 18.

(13) McMorris and Yost, *THIS JOURNAL*, 54, 2247 (1932).

values shows that they are in good agreement at the higher temperatures for all three runs, but at lower temperatures the values for Run II are considerably greater than those for the other runs. This deviation is due to the circumstance that the smaller partial pressures of some of the components in Run II are more sensitive to gas imperfections than is the case with Runs I and III.

In making the corrections for gas imperfections it must be borne in mind that it is not possible at this time to make exact estimates of the second virial coefficients for the individual gases present in the equilibrium mixtures, and, moreover, our knowledge of the interactions between the molecules of unlike gases is so incomplete that only crude estimates of them are possible. In the investigation of nitrosyl chloride⁹ it was possible to evaluate the magnitude of the imperfections in a fairly satisfactory manner. In the present case, since the relative amounts of nitric oxide, chlorine, and nitrosyl chloride were approximately the same as those in the investigation of nitrosyl chloride, and since the imperfections of nitrosyl bromide, bromine, and bromine chloride will doubtless be of the same order of magnitude as those of nitrosyl chloride and chlorine, it was decided to assume that the corrections would be equal to the same percentages of the total pressures as were found in the nitrosyl chloride equilibrium measurements. These percentages varied from 0.39% at 373°K. to 0.17% at 493°K.

The effect of applying the gas imperfection corrections is to reduce the abnormally high values of K' for Run II at the lower temperatures to values of K that are more nearly equal for the three runs. This indicates that the order of magnitude and nature of the correction has been correctly estimated. That the magnitudes and manner of making the corrections are not exactly correct is shown by the fact that, at the lower temperatures, the values of K are not sufficiently constant. Another factor causing the lack of constancy is the greater effect of experimental errors in the lower temperature range.

At 432°K. and above, the values of K for each run are nearly constant; they do show a tendency to increase slightly with temperature, but the increase is no greater than the variation from run to run. Inasmuch as the value of ΔH for the formation of bromine chloride from bromine and chlorine is certainly small, it is believed that the

TABLE III
RESULTS OF THE EQUILIBRIUM MEASUREMENTS

0°C. = 273.1°K. $K = P_{\text{Br}_2}P_{\text{Cl}_2}/P_{\text{BrCl}}^2$

Temp., °K.	Run I			Run II			Run III		
	P , cm.	K'	K	P , cm.	K'	K	P , cm.	K'	K
372.67	46.92	0.22	0.07	50.61	4.9	0.10	49.86	0.30	0.14
382.50	48.34	.19	.07	52.09	1.5	.13	51.50	.28	.15
392.31	49.78	.19	.08	53.63	0.63	.13	53.17	.29	.17
402.11	51.30	.18	.09	55.20	.46	.13	54.89	.24	.16
411.86	52.84	.18	.10	56.81	.32	.12	56.64	.23	.16
422.62	54.61	.16	.10	58.68	.22	.10	58.67	.21	.15
432.50	56.27	.16	.11	60.42	.24	.13	60.55	.20	.15
442.34	57.99	.16	.11	62.22	.22	.13	62.43	.20	.15
452.13	59.74	.16	.12	64.05	.21	.14	64.36	.20	.16
461.93	61.51	.17	.13	65.93	.22	.15	66.32	.20	.16
471.71	63.33	.17	.13	67.84	.22	.16	68.27	.19	.16
481.46	65.18	.17	.14	69.80	.22	.17	70.29	.20	.18
491.24	67.08	.18	.15	71.81	.22	.18	72.33	.21	.19

Mean of K for temperatures above 432°K. is 0.148 ± 0.011 , corresponding to a mean temperature of 462°K.

variations of K with temperature and from run to run are due principally to our inability to evaluate correctly the effect of gas imperfections and to experimental error.

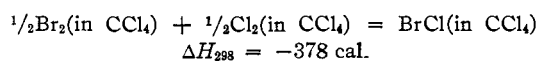
The Thermodynamic and Molecular Constants of Bromine Chloride.—The mean of the twenty-one values of K between 432 and 492°K. is $K = 0.148 \pm 0.011$, and this is probably a reliable value for the mean temperature of 462°K. The weighted mean of the values of K at room temperature (301°) is 0.126. On the very reasonable assumption that ΔH is effectively constant between 301 and 462°K., there results

$$\begin{aligned} \text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) &= 2\text{BrCl}(\text{g}) & (9) \\ \Delta H &= -270 \text{ cal.} & \Delta F_{298}^\circ = -1230 \text{ cal.} \\ & & \Delta S_{298}^\circ = 3.22 \text{ cal./deg.} & (10) \\ & & \Delta F_T^\circ &= -270 - 3.22T \end{aligned}$$

This free energy equation yields for 1100°K., the upper temperature employed by Schütza,⁶ $K = P_{\text{Br}_2}P_{\text{Cl}_2}/P_{\text{BrCl}}^2 = 0.18$, a value considerably higher than that reported, namely, 0.140. It might be supposed that ΔH is much smaller numerically than that calculated here, and that in addition the mean room temperature value of $K = 0.126$ has not been correctly estimated. In this event one would expect to obtain nearly the same value of K at all temperatures in the range investigated, namely, 0.14. Some of the results reported for room temperatures would be in accord with this supposition (Brauer and Victor⁵), while others would not (Vesper and Rollefson⁴).

An independent estimate of ΔH for reaction (9) was obtained by Blair and Yost,¹⁴ who measured the heat of the reaction

(14) Blair and Yost, *THIS JOURNAL*, **55**, 4489 (1933).



and, since the values of ΔH for the formation of $\text{ICl}(\text{g})$ and $\text{IBr}(\text{g})$ from the elements in the gaseous state are about 20% less than those found for the same reactions in carbon tetrachloride solutions, they suggested that ΔH for reaction (9) would be -600 cal. When our value of $K = 0.148$ at 462°K. is combined with that of Vesper and Rollefson, $K = 0.107$ at 301°K., the value calculated for ΔH is -570 cal. This in turn yields

$$\begin{aligned} \text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) &= 2\text{BrCl}(\text{g}) & (9) \\ \Delta F_{301} &= -1330 \text{ cal.} & \Delta H = -560 \text{ cal.} \\ \Delta S_{301} &= 2.56 \text{ cal. deg.} & \Delta F_T = -560 - 2.56T & (11) \end{aligned}$$

In order to decide between these three alternatives it is necessary to make use of the spectroscopic data for bromine, chlorine, and bromine chloride.

Spectroscopic Data.—The interatomic distances for Br_2 and Cl_2 are 2.28¹⁵ and 1.988 Å.,¹⁶ respectively, and their mean, 2.13 Å., will be assumed to be the interatomic distance for bromine chloride. This assumption conforms with the principle of the additivity of covalent radii.¹⁷ The vibrational frequency of bromine chloride was determined by Cordes and Sponer¹⁸ and is 430 cm.^{-1} . The internuclear distance, the frequency, and the values of K_{BrCl} lead to the following values for ΔH_0° , the heat content change at $T = 0$,

(15) Brown, *Phys. Rev.*, **39**, 777 (1932).
(16) Elliott, *Proc. Roy. Soc. (London)*, **123A**, 629 (1929). The value 1.988 Å. was recalculated by Professor R. M. Badger from Elliott's data.
(17) Pauling and Huggins, *Z. Krist.*, **87**, 205 (1934).
(18) Cordes and Sponer, *Z. Physik*, **79**, 170 (1932); see also Sponer, "Molekülspektren," Verlag von Julius Springer, Berlin, 1935, p. 18.

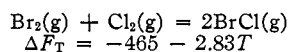
ΔS , and ΔH for the reaction under consideration. The necessary data for bromine were taken from the paper by Gordon and Barnes¹⁹ and for chlorine from Giauque and Overstreet.²⁰

TABLE IV
THERMODYNAMIC CONSTANTS FROM SPECTROSCOPIC AND
EQUILIBRIUM DATA

	Br ₂ (g) + Cl ₂ (g) = 2BrCl(g)		
<i>T</i> , °K.	301		462
ΔS° (spect.) cal./deg.	2.82		2.84
ΔH_0° cal.	-350 ^a	-470 ^b	-434 ^c
ΔH cal.	-366 ^a	-486 ^b	-443 ^c

^a $K_{\text{BrCl}} = 0.126$. ^b $K_{\text{BrCl}} = 0.107$. ^c $K_{\text{BrCl}} = 0.148$.

It is evident that ΔH_0° is more nearly constant when Vesper and Rollefson's room temperature value of K_{BrCl} is assumed. Accordingly the free energy equation 11 is more acceptable than 10. Inasmuch as the ΔS calculated from spectroscopic data is probably more reliable than that derived from equilibrium data alone, the following free energy equation can be regarded as best representing the data



(19) Gordon and Barnes, *J. Chem. Phys.*, **1**, 692 (1933).

(20) Giauque and Overstreet, *This Journal*, **54**, 1731 (1932).

We are indebted to Dr. D. P. Stevenson for making some of the calculations in this section.

Summary

Careful measurements on the gas phase equilibrium between nitric oxide, bromine, chlorine, nitrosyl chloride and bromide, and bromine chloride have been made in the temperature range 372 to 492°K. From the results, after an approximate correction for gas imperfections, the values of $K = P_{\text{Br}_2} P_{\text{Cl}_2} / P_{\text{BrCl}}^2$ were calculated. The mean value of K at 462°K. is 0.148 ± 0.011 .

This value of K was combined with the values obtained at room temperature by other investigators to calculate the heat content change ΔH attending the formation of two moles of bromine chloride. Three possible values were obtained, zero, -270 and -560 cal., depending on the room temperature value of K_{BrCl} selected. Spectroscopic data were employed to show that the probable value of ΔH is -465 cal. The most acceptable free energy equation for the reaction $\text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) = 2\text{BrCl}$, is $\Delta F_T = -465 - 2.83T$.

PASADENA, CALIF.

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[CONTRIBUTION FROM RESEARCH LABORATORIES, SHAWINIGAN CHEMICALS LTD.]

A Theory of Liquid Structure¹

BY ERNEST P. IRANY

That gases consist of free atoms or molecules in random motion and with a minimum of mutual interference, is elementary knowledge; that the truly solid, *i. e.*, the crystalline, state is distinguished by the geometrically regular arrangement of atoms, ions and electrons, has been established by X-ray analysis. The liquid state is transitory between these two forms of material constitution, but beyond this our knowledge is very vague.

The classical concepts do not provide an explanation for the obvious difference in physical appearance and the definite discontinuity between liquids and gases; we mostly think of a liquid in terms indistinguishable from those applied to a compressed gas. In crystals the molecular motion, due to the almost fixed positions of the molecules, is mainly vibratory, while in gases, on the contrary, translatory motion pre-

dominates. This classical distinction does not provide an explanation of the mobility and cohesion characteristic of the liquid state.

More recently, quantum theoretical considerations have been made the base of an approach to the problem. Formal solutions of some interest have been developed by statistical treatment but it hardly can be claimed that these solutions convey full comprehension of the liquid state.²

The problem can be solved only by assuming—no matter on what grounds—a definite concept of structure or molecular distribution, and by formulating it mathematically as an equation of the liquid state; the validity of the latter may then be proved by its ability to interpret and to repre-

(2) The question must be posed whether contemporary theory on liquid constitution rests on premises from which no conceivable molecular configuration is *a priori* excluded. If the primary concepts do not allow for, *e. g.*, the structure proposed in the present thesis—at least with some formal probability—no conclusions derived from them can claim uniqueness.

(1) Original manuscript received July 12, 1938.