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I The heat of formation of cementite as electrolyzed from a pure iron carbon alloy of eutectoid structure and composition II The signicicance of pH determinations in relation to hydrogen ion concentrations in mixed electrolyres [sic] III A proposed diagram for the ternary system iron-carbon-silicon

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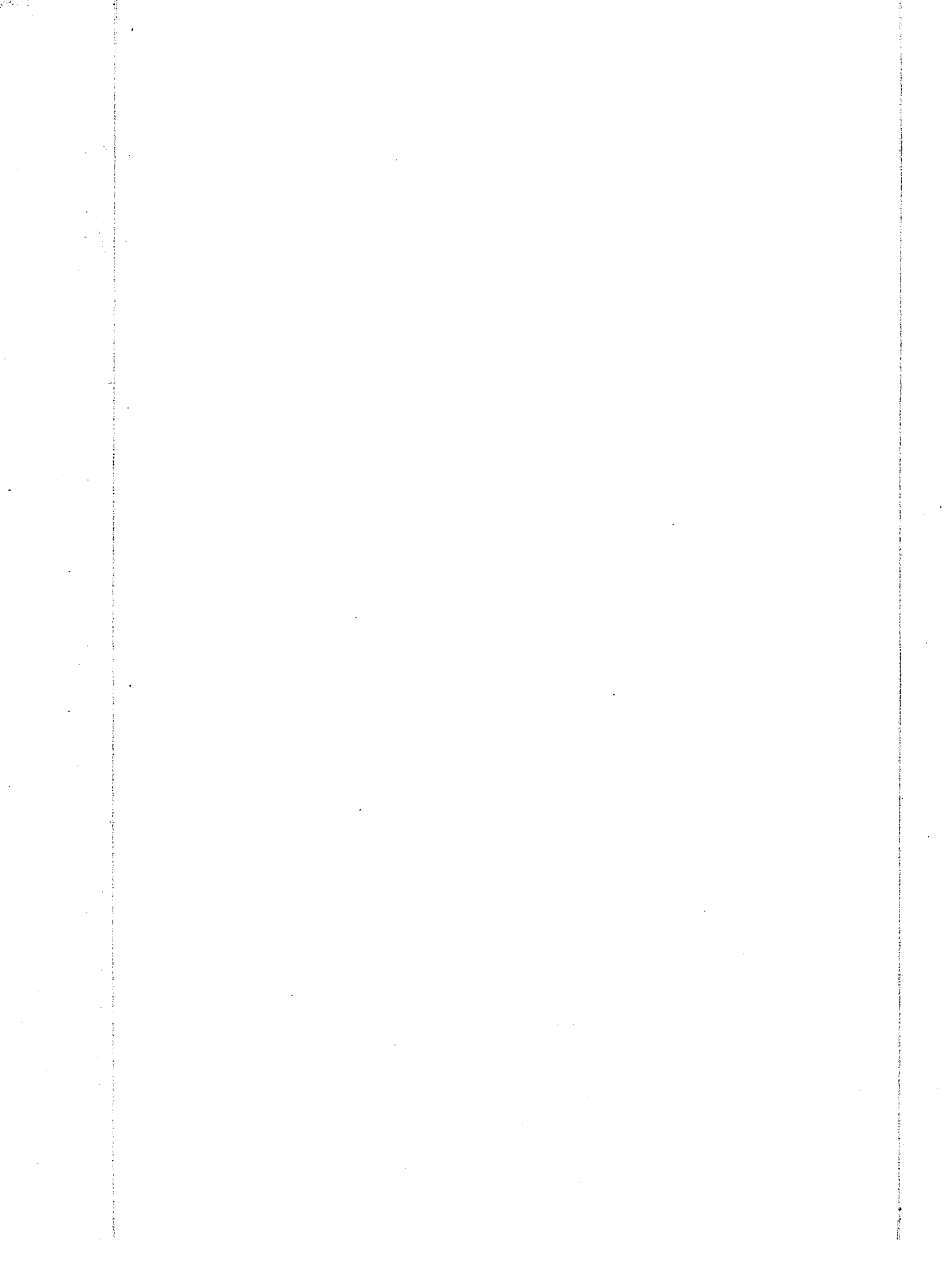
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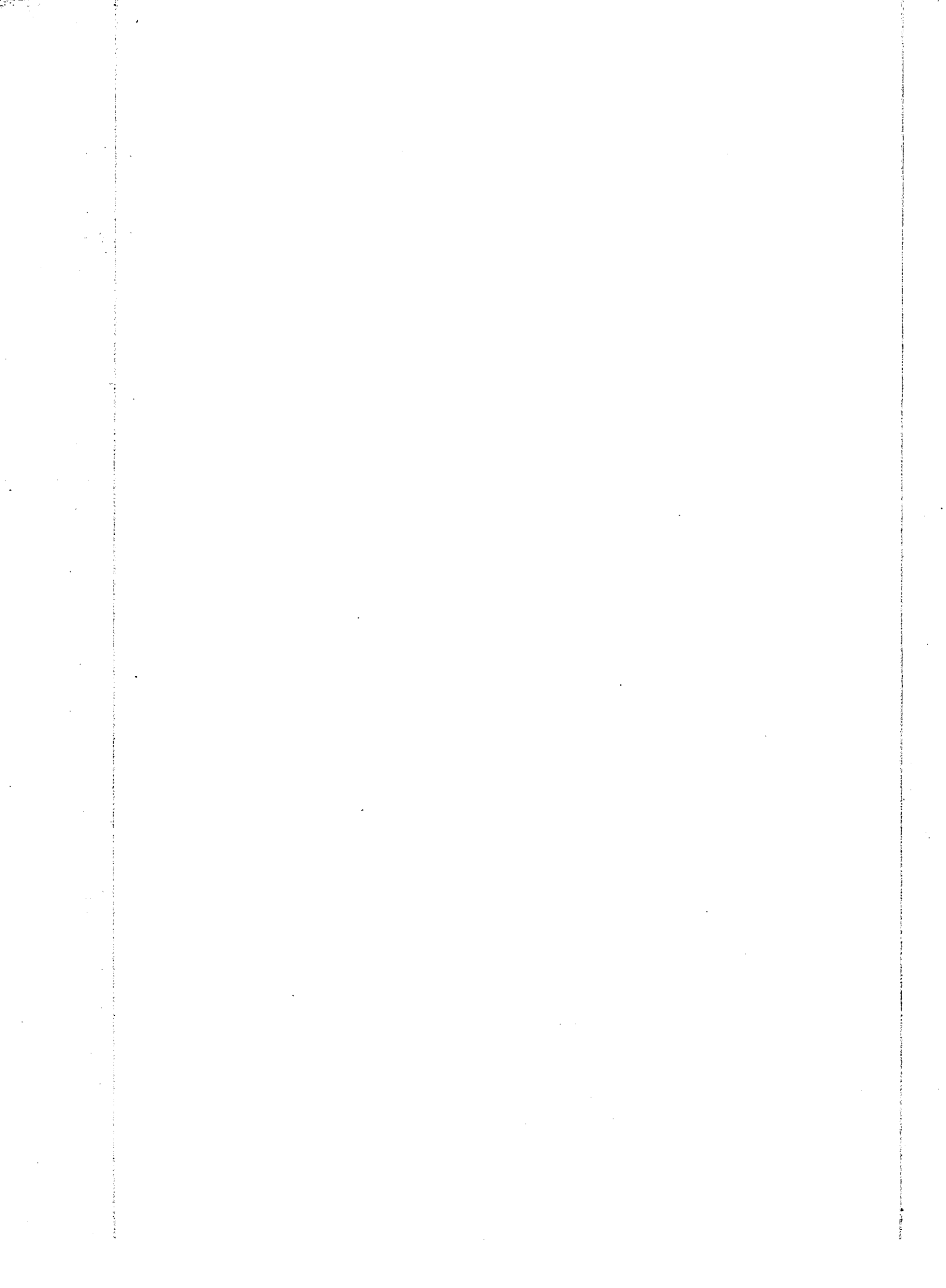
I. THE HEAT OF FORMATION OF CEMENTITE AS ELECTROLYZED
   FROM A PURE IRON CARBON ALLOY OF EUTECTOID STRUCTURE
   AND COMPOSITION

II. THE SIGNIFICANCE OF pH DETERMINATIONS IN RELATION
   TO HYDROGEN ION CONCENTRATIONS IN MIXED ELECTROLYRES

III. A PROPOSED DIAGRAM FOR THE TERNARY SYSTEM IRON-
   CARBON-SILICON

A Thesis Submitted

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for the Degree of

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I. THE HEAT OF FORMATION OF CEMENTITE AS ELECTROLYZED
FROM A PURE IRON CARBON ALLOY OF EUTECTOID STRUCTURE
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THEORETICAL CONSIDERATIONS

The treatment to determine the significance of pH determinations in relation to hydrogen ion concentrations in mixed electrolytes is more complicated for mixtures of higher order salts and for those having a common ion. However the consequences of the salt mixtures in regard to their influences on discrepances in the values of hydrogen ion concentrations as calculated from electromotive force measurements may be sufficiently illustrated by choosing a simple mixture.

In measuring pH a very common set up consists of the combination

$$H_2 (1 \text{ atm}), \; H^+ (C \text{ molal}), \; KCL \; (N), \; HgCl(s), \; Hg(1)$$
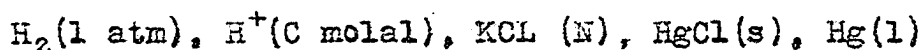
The electromotive force of the above cell is calculated by the formula

$$(1) \qquad E = 0.283 + 0.05915 \log \frac{1}{C_{H^+}}$$

where it is assumed that the electromotive force of the cell

$$H_2 (1 \text{ atm}), \; H^+ (C \text{ molal}) \; \| \; H^+ (1 \text{ molal}), \; H_2 (1 \text{ atm})$$

can be calculated by the formula

$$(2) \qquad E = 0.05915 \log \frac{1}{C_{H^+}}$$

It can be shown that if the acid in the two half cells acts as a perfect solute that these equations should give correct

results where we are dealing with a single highly ionized
acid as the electrolyte in solution.

For such a pure strong acid it has long been known that
the measured electromotive force does not agree with the
calculated electromotive force made from the above assumptions.
It was soon discovered that multiplying the concentration of
the electrolyte by the conductance ratio would not give
results and that the concentration of the electrolyte, when
multiplied by the degree of ionization as determined from
freezing point data and vapor pressure measurements, also
failed to give correct values for the electromotive force.

The immediate outcome of this discovery was an attempt
to measure something based upon the thermodynamic properties
of the solution that would calculate the correct value of the
electromotive force.

The view was taken that the chemical activity of the ion
might be proportional to its concentration or to the total
concentration of the dissolved acid. With the assumption that
this chemical activity was responsible for the electromotive
force it should be considered a corrected concentration which
could be substituted for the actual concentration and which
would give the correct electromotive force. This was done as
follows: Let a be the corrected concentration and c the actual
concentration, then define the relation of a to c by the
equation

$$(3) \qquad\qquad a = c\gamma$$

Thus γ may be considered as the thermodynamic degree of ion-
ization. This analogy holds for a solution of a strong

uni-univalent electrolyte it its pure water solution for quite low concentrations but fails completely at higher concentrations of a single strong electrolyte such as hydrochloric acid solutions and for complex salt mixtures. Now evidently the ratio of the activity of an ion in one solution to its activity in any other solution may be calculated by the equation

$$(4) \qquad E = \frac{RT}{F} \ln \frac{\alpha_1}{\alpha_2}$$

whenever it is possible to measure the electromotive force.

Since all such solutions at sufficiently high dilution show $\alpha_{H^+} = C_{H^+}$ it means that $\gamma = 1$ wherever the behavior is that of a perfect solution. The value of C_{H^+} which gives a value of unity to α_{H^+} has been chosen as the reference state and in fact corresponds to the concentration which produces the standard electrode potential.

The equation

$$(5) \qquad E = 0.283 + 0.05915 \log \frac{1}{\alpha_{H^+}}$$

thus results. It may now be stated that the pH measured correctly signifies $\ln \frac{1}{\alpha_{H^+}}$ rather than $\ln \frac{1}{C_{H^+}}$, since $\alpha_{H^+} = C_{H^+}$.

When, however, mixed electrolytes are considered the behavior is so different from that which has been assumed in the use of the hydrogen electrode that it should be carefully considered. As an example of the misinterpretation of the results of such measurements, some of the best known workers in the biological field still consider that the potential of the hydrogen electrode is influenced only by the hydrogen ion concentration.

In order to obtain as broad an understanding as possible of the principle which seems to govern the activity of such an ion as the hydrogen ion more comprehensive definitions of α , m , and γ as given by G. N. Lewis[1] will be used.

In general it is necessary to define α by the equation

(6) $$\alpha_{\pm} = (\alpha_{+}^{\nu_{+}} \alpha_{-}^{\nu_{-}})^{1/\nu} = \alpha_{z}^{1/\nu}$$

where ν is the total number of ions formed from a formula weight of the salt, ν_{+} being the number of positive ions and ν_{-} being the number of negative ions. Thus $\nu = \nu_{+} + \nu_{-}$

m is defined by the equation

(7) $$m_{\pm} = m(\nu_{+}^{\nu_{+}} \nu_{-}^{\nu_{-}})^{1/\nu} = (m\nu_{+}^{\nu_{+}} m\nu_{-}^{\nu_{-}})^{1/\nu} = (m_{+}^{\nu_{+}} m_{-}^{\nu_{-}})^{1/\nu}$$

and

(8) $$\gamma = \frac{\alpha_{\pm}}{m_{\pm}} = \left[\left(\frac{\alpha_{+}}{m_{+}}\right)^{\nu_{+}} \left(\frac{\alpha_{-}}{m_{-}}\right)^{\nu_{-}} \right]^{1/\nu} = (\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}})^{1/\nu}$$

These definitions are so taken in order to allow γ to approach unity at infinite dilution for any salt of any type from the simplicity of NaCl to that of salts more complex than $La_2(SO_4)_3$ For salts of the type NaCl $\alpha_{\pm} = (\alpha_{Na^+}\alpha_{Cl^-})^{1/2} = \alpha_{z}^{1/2}$. If the solution be sufficiently dilute so that the activity of the two ions Na^+ and Cl^- may be considered equal $\alpha_{\pm} = \alpha_{Na^+} = \alpha_{Cl^-}$ and $m_{\pm} = m_{NaCl}$, whence $\gamma = \frac{\alpha_{Na^+}}{m_{NaCl}}$ which is identical with the definition of the thermodynamic degree od ionization given above.

The fact has been long recognized that the influence of the electrical charges upon the ions was largely responsible for the properties of the ions as well as that of

the solvent. In fact there is a rather complete treatment of solutions from that standpoint which is at least partially successful. Out of this fact Lewis developed a quantity which he calls the ionic strength. In any solution of strong electrolytes let us multiply the stoichiometrical molality of each ion by the square of its valence (or charge). The sum of these quantities, divided by two (since we have included both positive and negative ions) we call the ionic strength, and designate by μ. Thus in general we have

$$\mu = \frac{m_1^+ \, \nu_1^+ \, n_1^{+2} + m_1^- \, \nu_1^- \, n_1^{-2} + m_2^+ \, \nu_2^+ \, n_2^{+2} + m_2^- \, \nu_2^- \, n_2^{-2}}{2}$$

where the subscripts refer to solutes 1, 2, etc., regardless of whether or not there are present common ions. For a mixture of uni-univalent electrolytes such as HCl and KNO_3 we get

$$\mu = \frac{m_1 \, (1)^2 + m_1 \, (1)^2 + m_2 \, (1)^2 + m_2 \, (1)^2}{n} = m_1 + m_2$$

For a mixture such as HCl and CaCl we get

$$\mu = \frac{m_1 \, (1) + m_1 \, (1) + m_2 \, (2) + m_2 \, (2)}{2} = m_1 + 3m_2$$

The important principle known as the principle of the ionic strength is that in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength. Moreover since it is true that the activity coefficient of a certain strong electrolyte is independent of the particular character of any other strong electrolyte which may be present but depends solely

upon the total ionic strength, the same principle should apply
to the individual ions unless as Lewis says, some other
peculiar compensation operates. Therefore we may state that
in dilute solutions of any strong electrolytes, the activity
coefficient of any individual ion depends solely upon the total
ionic strength of the solution.

When the solubility of a slightly soluble uni-univalent
salt like TlCl is studied in the presence of strong electro-
lytes like HCl, KCl, KNO$_3$, and K$_2$SO$_4$ the relation between $\mu^{1/2}$
and $\frac{1}{m_\pm}$ is as shown in Fig. 1. The data from which this
graph was constructed are given in Table I and are based upon
the solubility measurements of Bray and Winninghoff[2].
This treatment of solubility measurements is exactly that
given on page 371 of Lewis and Randall's Thermodynamics. The
important thing to note about the graph in Fig. 1 is that up
to a value of $\mu^{1/2}$ equal to 0.17 all the curves fall together
in a straight line.

In the case of the solubility of TlCl given above, in
each solution of mixed electrolytes the solution was saturated
with TlCl and therefore $a_\pm$ remained constant. Thus from the
relation $\gamma = \frac{a_\pm}{m_\pm}$ we see that γ is inversely propor-
tional to $m_\pm$. Taking the slope of that part of the graph
that is a straight line to be $-k$, we obtain the simple equation

(9) $$\frac{a_\pm}{m_\pm} = 1 - k\mu^{1/2} = \gamma$$

Since the value of γ for a given μ does not depend upon
either the presence or absence of a solid phase we may apply
a similar treatment to any mixture of strong electrolytes

providing we keep $a \pm$ constant. This restriction is necessary in order that a graph of the form corresponding to the one in Fig. 1 be obtained.

The treatment applied to mixtures of strong electrolytes as presented in this paper may be divided into two parts:

FIRST PART. HCl IN THE PRESENCE OF ANY STRONG ELECTROLYTE WITHOUT A COMMON ION.

SECOND PART. HCl IN THE PRESENCE OF ANY STRONG ELECTROLYTE WITH A COMMON ION.

In each part calculations have been made to determine

A. The Relation between m_{HCl} and m_z, a_{H^+} being held constant.

B. The relation between a_{H^+} and m_{HCl}, m being held constant.

FIRST PART

A. THE RELATION BETWEEN m_{HCl} AND m_z, $\alpha\pm$ BEING HELD CONSTANT IN THE CASE OF HCl IN THE PRESENCE OF ANY STRONG ELECTROLYTE WITHOUT A COMMON ION.

The data upon which this part of the calculations have been made are taken from the Table of Activities In Aqueous Hydrochloric Acid Solutions as given on page 336 of Lewis and Randall's Thermodynamics. Those values which have been used are given in Table II. These data are for pure aqueous solutions of HCl, therefore $m_{HCl} = \mu$ and thus from these data the graph as shown in Fig 2 has been constructed.

In the present case $m_{HCl} = m\pm$ and assuming $\alpha_{\pm} = \alpha_{H}^{+} = \alpha_{Cl}^{-}$, equation (9) can be written in the form

(10)
$$\frac{\alpha_{H}^{+}}{m_{HCl}} = \gamma = 1 - k\mu^{1/2}$$

From Table II taking corresponding values of γ and μ and substituting them in equation (10) the value of k is obtained. Such a set of calculations is as follows:

$$k = (1 - 0.992)\frac{1}{(0.0005)^{1/2}} = 0.35777$$

$$k = (1 - 0.984)\frac{1}{(0.001)^{1/2}} = 0.50596$$

$$k = (1 - 0.971)\frac{1}{(0.002)^{1/2}} = 0.64846$$

$$k = (1 - 0.947)\frac{1}{(0.005)^{1/2}} = 0.74953$$

$$k = (1 - 0.924)\frac{1}{(0.01)^{1/2}} = 0.76$$

From the above calculations k is found to vary and since in the case of TlCl $\alpha\pm$ was constant whereas all other quantities

changed, it follows that the value of k is determined by the
particular value of $\alpha\pm$. The above values of k and the corre-
sponding values of $\alpha\pm$ are recorded in Table II, and the graph
of these quantities is shown in Fig. 2A.

Since $\alpha = m_1 + m_2$ for a simple mixture like HCl and KNO_3
equation (10) can be written in the form.

$$(11) \quad m_2 = \frac{m_{HCl}^2 - 2m_{HCl}\,\alpha_{H^+} + \alpha_{H^+}^2}{m_{HCl}^2\,k^2} - m_{HCl}$$

Now the above equation (11) can be used to calculate
values of m_2 corresponding to chosen values of m_{HCl}, α
held constant by simply substituting the chosen values of m_{HCl}
and a value of $\alpha\pm$ with the corresponding k. Such a set of
calculations are here shown.

$$m_2 = \frac{(0.51 \times 10^{-3})^2 - 2(0.51 \times 10^{-3})(0.000496)+(0.000496)^2}{(0.51 \times 10)\ (0.35777)}$$

$$-(0.51 \times 10^{-3}) = 0.0051971$$

$$m_2 = \frac{(1.1 \times 10^{-3})^2 - 2(1.1 \times 10^{-3})(0.000984)+(0.000984)^2}{(1.1 \times 10^{-3})^2 (0.50596)^2}$$

$$-(1.1 \times 10^{-3}) = 0.004234$$

$$m_2 = \frac{(2.1 \times 10^{-3})^2 - 2(2.1 \times 10^{-3})(0.001942)+(0.001942)^2}{(2.1 \times 10^{-3})^2 (0.64846)^2}$$

$$-(0.21 \times 10^{-3}) = (0.01138)$$

$$m_2 = \frac{(5.5 \times 10^{-3})^2 - 2(5.5 \times 10^{-3})(0.00474)+(0.00474)^2}{(5.5 \times 10^{-3})^2 (0.74953)^2}$$

$$-(5.5 \times 10^{-3}) = 0.028538$$

$$m_2 = \frac{(11 \times 10^{-3})^2 - 2(11 \times 10^{-3})(0.00924) + (0.00924)^2}{(11 \times 10^{-3})^2 (0.76)^2}$$

$$- (11 \times 10^{-3}) = 0.033321$$

The results of such a series of calculations are given in Table III, and the relation between m_{HCl} and m_2 at various values of $\alpha\pm$ are shown in Fig. 3.

FIRST PART

B. THE RELATION BETWEEN $\alpha_\pm$ AND m_{HCl}, μ BEING HELD CONSTANT IN THE CASE OF HCl IN THE PRESENCE OF ANY STRONG ELECTROLYTE WITHOUT A COMMON ION.

Writing equation (9) in the form

(12) $\alpha_\pm + m_{HCl} \mu^{1/2} k = m_{HCl}$

and noting that k is a function only of $\alpha_\pm$ it follows that for each particular value of $\alpha_\pm$ this equation may be written in the more general form

(13) $\alpha_\pm + xk = y$

This equation is the equation of a straight line whose intercept is $\alpha_\pm$ and whose slope is equal to k. Thus different values of $\alpha_\pm$ give a set of straight lines with intercepts equal to $\alpha_\pm$ and of different slope as shown in Fig. 4. Considering the form of equation (13) and the fact that k is a function only of $\alpha_\pm$ it is evident that the values of x and $\alpha_\pm$ may be arbitrarily chosen. Thus taking from Fig. 2A values of k corresponding to the chosen values for $\alpha_\pm$ the value of the expression $\alpha_\pm + xk$ is obtained. This with the chosen x determine one point on a particular line. Such a series of points together with the corresponding intercepts $\alpha_\pm$ serve to fix the position of each line in the graph of Fig. 4.

The graph in Fig. 4 is used to evaluate values of $\alpha_\pm$ corresponding to chosen values of m_{HCl} at a given μ as follows. Suppose it is desired to determine when $m_{HCl} = 0.0007$ and $\mu = 0.04$. Substituting these values in equation (12) there results

$$\alpha_\pm = (0.007)(0.04)^{1/2} \quad k = 0.007$$

whence $x = 0.0014$ and $\alpha_\pm + xk = 0.007$. Now locating this point on the graph in Fig. 4, then moving downward and parallel to the nearest line of constant $\alpha_\pm$ until the abscissa is reached the value of $\alpha_\pm$ is obtained. The results of this series of calculations are given in Table V and a graph of $\alpha_\pm$ against m_{HCl} is shown in Fig. 5. Since the slope of the lines in this graph correspond to the value of $\frac{1}{\gamma}$ at the particular value of μ we have for the values of γ, 0.932, 0.888 and 0.852 when μ has the respective values 0.01, 0.0225 and 0.04. According to the original data these values should be 0.924, 0.887 and 0.866. Hence these values are within the limits of accuracy with which values may be taken from the graph in Fig. 4.

SECOND PART

A. THE RELATION BETWEEN m_{HCl} AND m_z, α_{H^+} BEING CONSTANT IN THE CASE OF HCl IN THE PRESENCE OF ANY STRONG ELECTROLYTE WITH A COMMON ION.

In the case of a mixture of uni-univalent electrolytes such as HCl and KCl there exists the simple relation

$$(14) \qquad m_{HCl} = \frac{m_{\pm}^2}{\mu}$$

since $m_{\pm} = \left[(m_{HCl})(m_{HCl} + m_z) \right]^{1/2}$ and $\mu = m_{HCl} + m_z$. likewise for a mixture of bi-bivalent ions such as $BaCl_2$ and $CaCl_2$ there exists the simple relation

$$m_{BaCl_2} = \frac{3m_{\pm}^3}{2\mu}$$

since $m_{\pm} = \left[(m_{BaCl_2})(2m_{BaCl_2} + 2m_{CaCl_2}) \right]^{1/3}$ and $\mu = 3(m_{BaCl_2} + m_{CaCl_2})$ However in the case of mixtures of electrolytes of different types no such simple relation exists and a treatment different from that which follows must be used.

To calculate the value of m_z for a given value of m_{HCl}, $\alpha_{\pm}$ being held constant the values of γ and $\mu^{1/2}$ have been taken from Table I and plotted as shown in Fig. 5A. The same straight line graphs are shown separately in Figures 6, 7, 8 and 9. Since each of these graphs is for a particular value of $\alpha_{\pm}$ we may read off values of γ or $\frac{\alpha_{\pm}}{m_{\pm}}$ for different values of μ and then calculate $m_{\pm}$. From the values of $m_{\pm}$ and μ is is possible to calculate the corresponding values of m_{HCl} and m_z as shown below.

From the graph in Fig. 6 ($\alpha_\pm = 0.000496$) it is found that for $\mu^{1/2} = 0.1$, $\gamma = \dfrac{\alpha_\pm}{m_\pm} = 0.9657$, therefore

$$m_{HCl} = \frac{m_\pm^2}{\mu} = \frac{\left[\dfrac{0.000496}{0.9657}\right]^2}{0.01} = 0.00002638$$

and $m_z = 0.00997362$

From the graph in Fig. 7 ($\alpha_\pm = 0.000984$) it is found that for $\mu^{1/2} = 0.15$, $\gamma = \dfrac{\alpha_\pm}{m_\pm} = 0.9237$, therefore

$$m_{HCl} = \frac{m_\pm^2}{\mu} = \frac{\left[\dfrac{0.000984}{0.9237}\right]^2}{0.0225} = 0.00005055$$

and $m_z = 0.02244945$

From the graph in Fig. 8b ($\alpha_\pm = 0.001942$) it is found that for $\mu^{1/2} = 0.2$, $\gamma = \dfrac{\alpha_\pm}{m_\pm} = 0.87$, therefore

$$m_{HCl} = \frac{m_\pm^2}{\mu} = \frac{\left[\dfrac{0.001942}{0.87}\right]^2}{0.04} = 0.0001245$$

and $m_z = 0.398755$

From the graph in Fig. 9 ($\alpha_\pm = 0.00474$) it is found that for $\mu^{1/2} = 0.125$, $\gamma = \dfrac{\alpha_\pm}{m_\pm} = 0.9066$, therefore

$$m_{HCl} = \frac{m_\pm^2}{\mu} = \frac{\left[\dfrac{0.00474}{0.9066}\right]^2}{0.015625} = 0.0017495$$

amd $m_z = 0.0138755$

The results of this series of calculations are given in
Tables VI, VII, VIII and IX and the corresponding graphs are
shown in Figures 6A, 7A, 8A and 9A. In the Figures 6, 7, 8
and 9 the relation of m_{HCl} to $\mu^{1/2}$ has been plotted and gives
the curves there shown.

SECOND PART

B. THE RELATION BETWEEN $\alpha_{H}+$ AND m_{HCl}, μ BEING HELD CONSTANT
IN THE CASE OF HCl IN THE PRESENCE OF ANY STRONG ELECTROLYTE
WITH A COMMON ION.

By using a procedure similar to the one used in the
case of an electrolyte without a common ion the value of $\alpha_{\pm}$
for a given value of $m_{\pm}$ can be found. Thus if $\mu = 0.0025$ and
$m_{HCl} = 0.0005$, then $m_2 = 0.002$ and $m_{\pm} = 0.001118$. Substi-
tuting these values in equation (12) there results

$$\alpha_{\pm} + (0.001118)(0.0025)^{1/2} k = 0.001118$$

It is seen that $x = 0.0000559$ and that $\alpha_{\pm} + xk = 0.001118$.
Locating this point on the graph in Fig. 4 and then moving down-
ward and parallel to the nearest line of constant $\alpha_{\pm}$ until the
abscissa is reached the value of $\alpha_{\pm}$ is found to be 0.00107.
The results of such a series of calculations are given in Table
X.

In order to determine the value of $\alpha_{H}+$ consider the principle
of the ionic strength as applied to the ions. At a given total
ionic strength each ion has a definite activity coefficient   .
Such a Table of activity coefficients of individual ions at
various values of μ is given on page 382 of Lewis and Randall's

Thermodynamics. Those values which are of use here have been recorded in Table IIA and a graph is shown in Fig 2. It should be noticed that for values of μ considered here all the ions mentioned in Table IIA have the same activity coefficient for a given .

Hence it matters not in dilute solutions whether HCl is in the presence of a electrolyte with or without a common ion, the activity coefficient of the hydrogen ion will depend solely upon the total ionic strength and therefore the activity of the hydrogen ion will be $\gamma_{H^+} m_{HCl}$. Taking values for γ_{H^+} from Table IIA and vlaues for m_{HCl} from Table X there is obtained the values of α_{H^+} as shown in the last column of Table X. When these values of α_{H^+} are plotted against the corresponding values for m_{HCl} the graph shown in Fig. 10 results while if α_{H^+} is plotted against corresponding values of $m_{\pm}$ the graph in Fig. 11 is obtained.

In case the solution is not sufficiently dilute so that the principle of the ionic strength may be applied to the individual ions but does hold as applied to the electrlyte the value of α_{H^+} must be determined by some other method which determines α_{H^+} directly or else gives a value for α_{Cl} from which in combination with $\alpha_{\pm}$ the value of α_{H^+} may be obtained/

CONCLUSION

The conclusions which follow are all stated with the assumption of the validity of the principle of the ionic strength.

In a hydrogen electrode set-up consisting of a normal calomel electrode and a hydrogen electrode, with the liquid potentials properly cared for, the value of the measured electromotive force is given by the equation

$$(15) \qquad E = 0.283 + 0.05915 \log \frac{1}{\alpha_{H^+}}$$

It follows that since a large number of different values of m_{HCl} may accompany a constant value of α_{H^+}, as shown in the graphs of Figures 5 and 10, the determination of α_H by the ordinary hydrogen ion set up does not determine the value of m_{HCl} unless the value of μ is already known.

It is very likely that the investigator in any field will be more concerned with the value of α_{H^+} rather than with that of m_{HCl} since the chemical effects of the hydrogen ion would be expected to bear a closer relation to α_H^+ than to m_{HCl}.

Since the value of the electromotive force as calculated from equation (15) does not determine the value of m_{HCl} where the principle of the ionic strength holds and since at higher ionic strengths variations from the principle of the ionic strength occur in almost every way it follows that the hydrogen electrode cannot be expected to determine the value of m_{HCl} or

of any other acid in highly complex mixtures.

These results have been readily subject to prediction since the time that the discovery of the principle of the ionic strength was announced

Table.I. Solubility of Thallous Chloride at 25 in the presence of other salts.

m_{KNO_3}	m_{TlCl}	$m_{\pm}$	$\dfrac{1}{m_{\pm}}$	μ	$\mu^{1/2}$
0	0.01607	0.01607	62.228	0.01607	0.12677
0.02	0.01716	0.01716	58.275	0.03716	0.19277
0.05	0.01826	0.01826	54.764	0.06826	0.26127
0.1	0.01961	0.01961	50.995	0.11961	0.34189
0.3	0.02313	0.02313	43.234	0.32313	0.56844
1	0.03072	0.03972	32.552	1.03072	1.10152
m_{KCl}					
0.025	0.00869	0.017078	58.554	0.03369	0.18352
0.5	0.0059	0.018161	55.964	0.0559	0.23643
0.1	0.00396	0.02029	49.285	0.10396	0.32243
0.2	0.00268	0.023307	42.907	0.20268	0.4592
m_{HCl}					
0.025	0.00866	0.017058	58.624	0.03366	0.1833
0.05	0.00583	0.018042	55.426	0.05583	0.23628
0.1	0.00383	0.019942	50.146	0.10383	0.32223
0.2	0.00253	0.022172	44.177	0.20253	0.45003
$m_{K_2SO_4}$					
0.02	0.01779	0.01779	56.211	0.7777	0.27891
0.05	0.01942	0.01942	51.493	0.16942	0.41161
0.1	0.02137	0.02137	46.795	0.32137	0.5669
0.3	0.026	0.026	38.461	0.926	0.96228
1	0.03416	0.024416	29.274	3.03216	1.7413
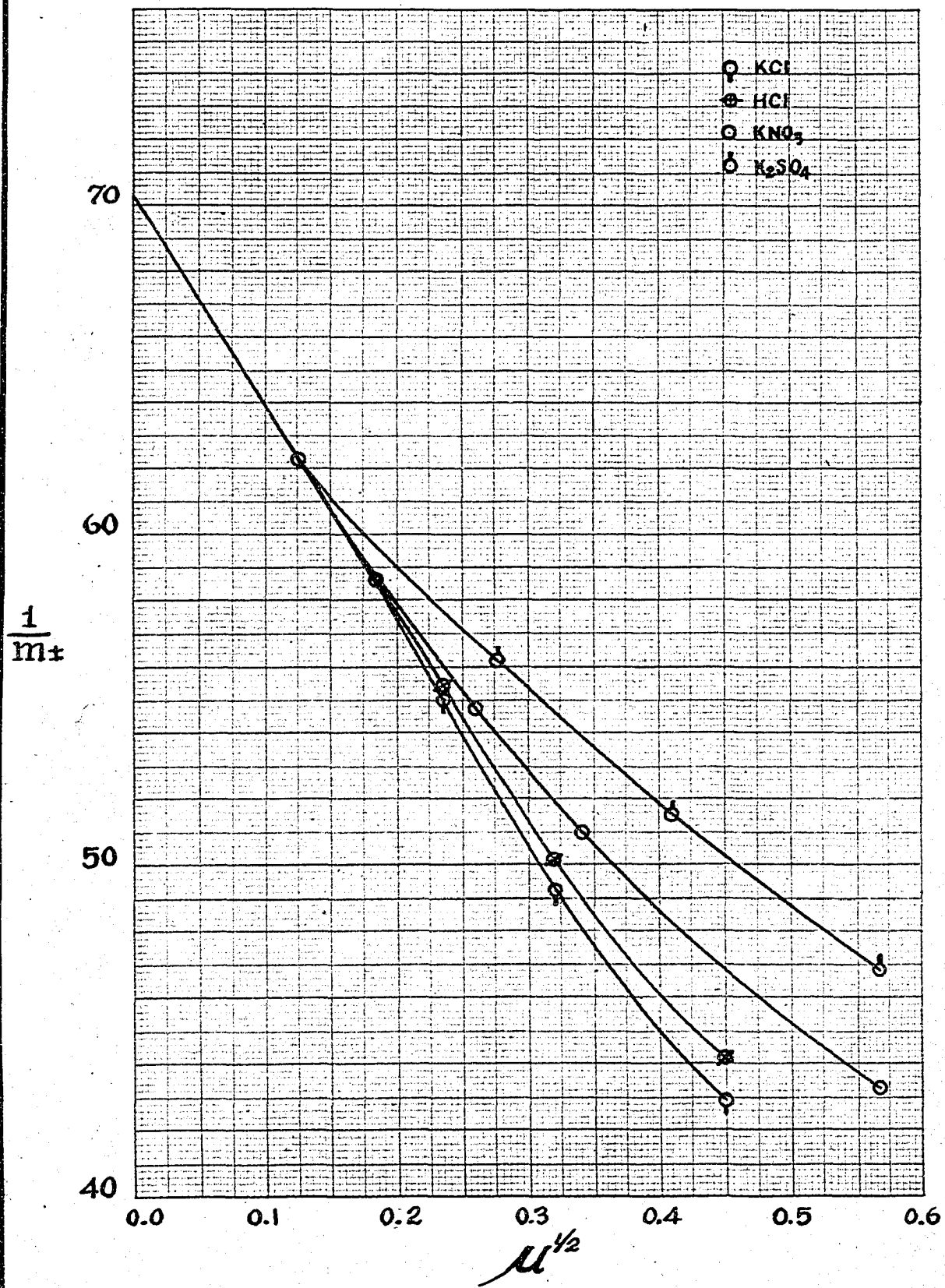
Fig. 1.

Table II. Activities In Aqueous Hydrochloric Acid Solutions.

m_{HCl}	$\mu^{1/2}$	γ	$\alpha_\pm$	k
0.0005	0.022361	0.992	0.000496	0.35777
0.001	0.031323	0.984	0.000984	0.50596
0.002	0.044721	0.971	0.001942	0.64846
0.005	0.070711	0.947	0.00474	0.74953
0.01	0.1	0.924	0.00924	0.76
0.02	0.14142	0.894	0.01788	
0.05	0.22361	0.86	0.043	
0.1	0.31623	0.814	0.0814	
0.2	0.44721	0.783	0.1566	
0.5	0.70711	0.762	0.381	

Table IIA. Activity Coefficients Of Individual Ions At
Various Values Of The Ionic Strength.

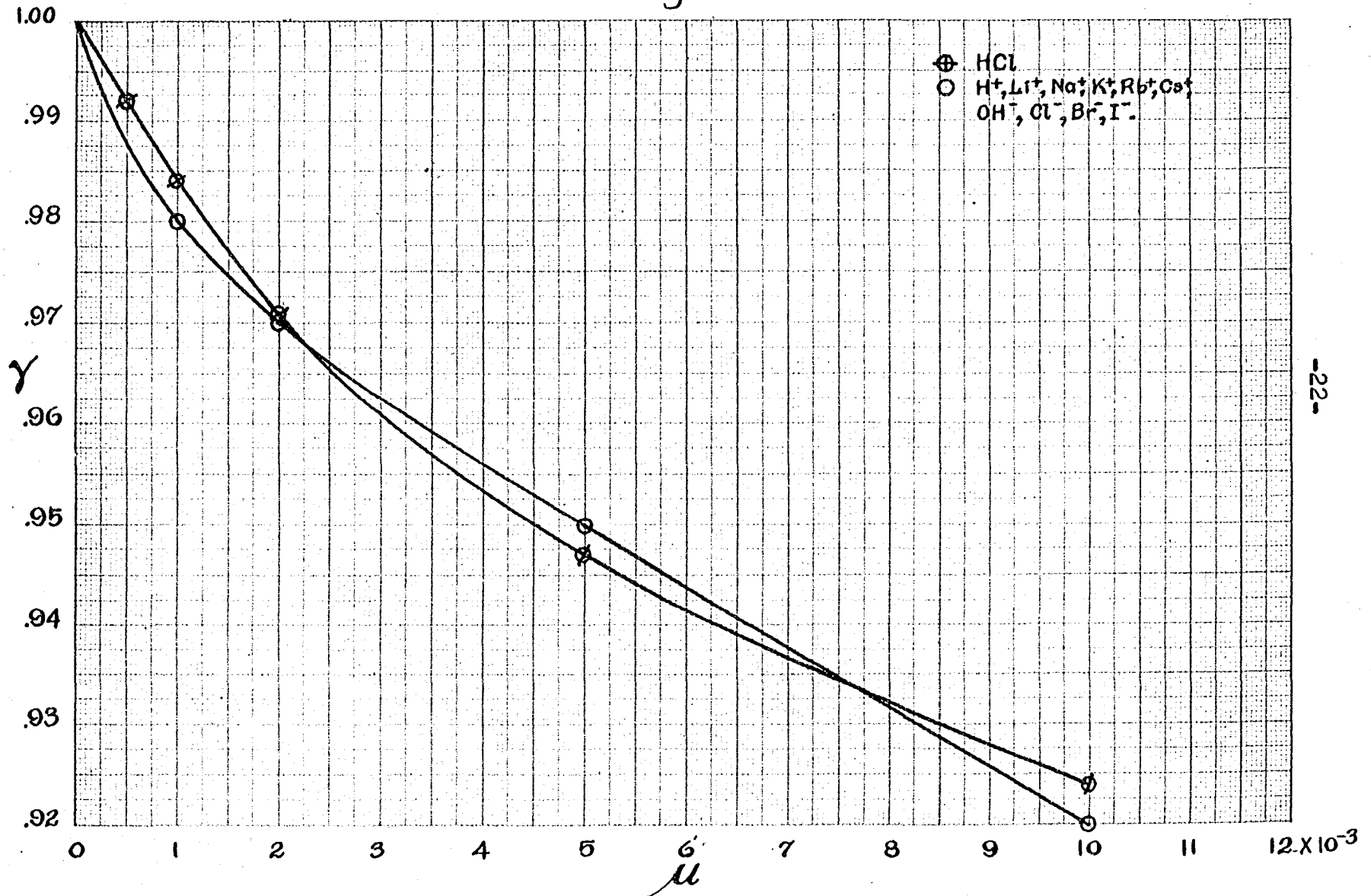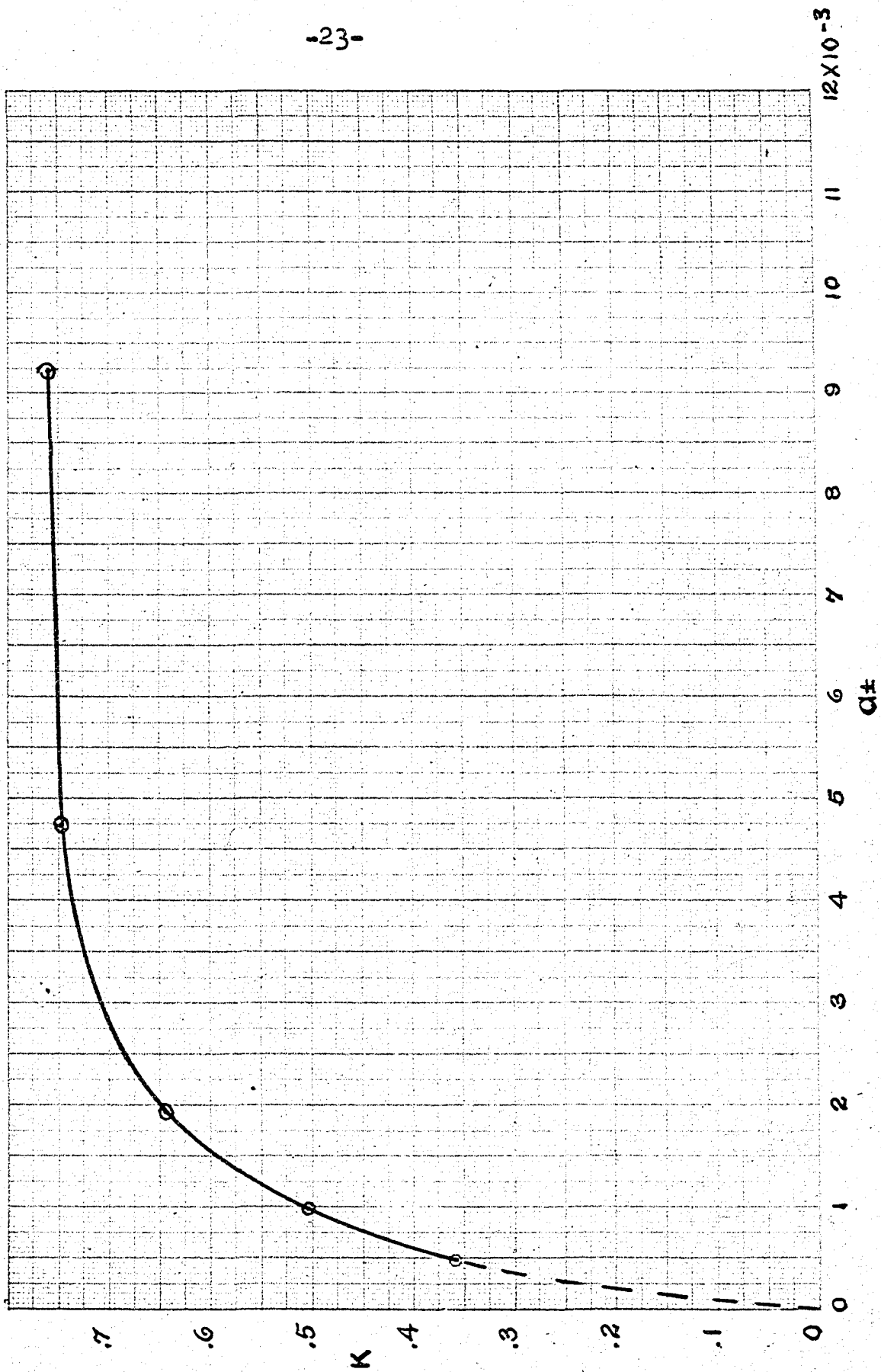| μ	0.001	0.002	0.005	0.01	0.02
H^+	0.98	0.97	0.95	0.92	0.90
OH^-	0.98	0.97	0.95	0.92	0.89
$Cl^-, Br^-, I^-,$	0.98	0.97	0.95	0.92	0.89
Li^+	0.98	0.97	0.95	0.92	0.89
Na^+	0.98	0.97	0.95	0.92	0.89

Fig. 2.

Fig. 2A.

Table III. The Relation Between m_{HCl} And m_2 At Various Values of $\alpha\pm$. No Common Ion Present.

$\alpha\pm$ (10^{-3})	0.496	0.984	1.942	4.74	9.24
m_{HCl}(10^{-3})	(- - - - - - - - - - - - - - -	- - - - -	m_2 - - - - - -	- - - - - - - - - -)	
0.51	0.00519				
0.52	0.01594				
0.53	0.03145				
0.54	0.05117				
0.55	0.07461				
0.56	0.10133				
0.57	0.13097				
0.58	0.16315				
0.59	0.19818				
0.6	0.234				
0.7	0.66274				
0.8	1.1273				
0.9	1.5733				
1.0	1.9835				
1.1		0.04234			
1.2		0.12536			
1.3		0.22951			
1.4		0.34351			
1.5	3.4986	0.46075			
1.6		0.57607			
1.7		0.69123			
1.8		0.80098			
1.9		0.90602			
2	4.4161	1.00603			
2.1			0.01138		

|					
2.3			0.05533		
2.5			0.11599		
2.8			0.22951		
3	5.4373	1.761			
3.5			0.46773		
4	5.9913	2.2168	0.62911		
5	6.3345	2.5151	0.88454		
5.5				0.028538	
6	6.5533	2.7241	1.0818	0.081398	
6.5				0.124	
7	6.7378	2.8782	1.2346		
8	6.8892	2.9964	1.3557		
9	6.9663	3.0898	1.4535		
10	7.0469	3.1654	1.5341	0.4825	
11					0.03332
12					0.07958
13					0.13183
14					0.18614
15				0.81781	0.24029
16					0.29305
17					0.34375
18					0.3974
19					0.43784
20	7.4099	3.5114	1.9187	1.0162	0.48113
21					0.52194
22					0.56042
30	7.5266	3.6243	2.0502	1.232	0.79904
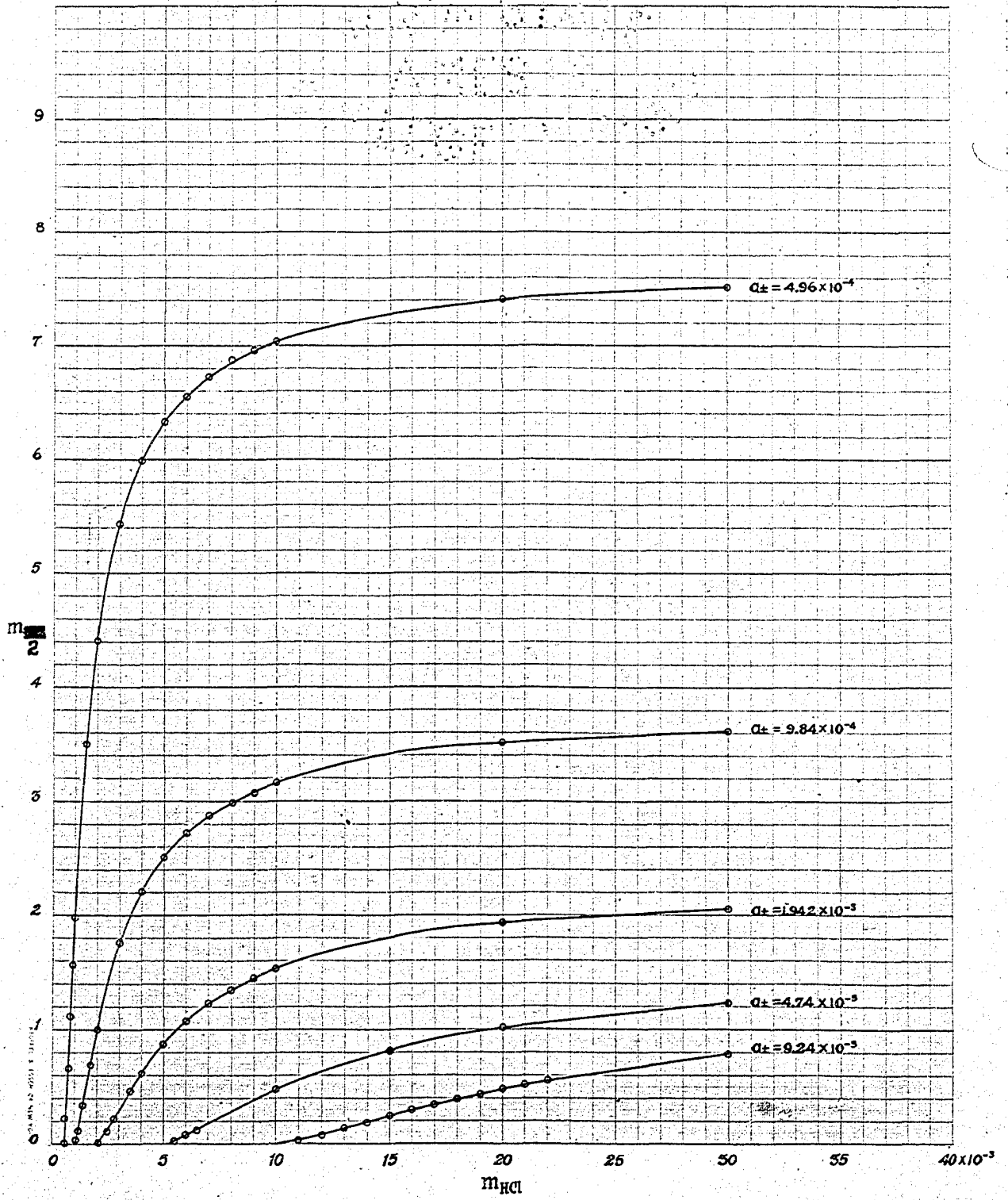
Fig. 3.

Table IV. Values of $\alpha_\pm$ and $\alpha_\pm + xk$ when x has the value 0.001.

$\alpha_\pm (10^{-3})$	k	$\alpha_\pm + xk (10^{-3})$	$\alpha_\pm (10^{-3})$	k	$\alpha_\pm + xk (10^{-3})$
0.5	0.365	0.865	5.5	9.749	6.249
1	0.508	1.508	6	0.751	6.751
1.5	0.592	2.092	6.5	0.753	7.253
2	0.65	2.65	7	0.754	7.754
2.5	0.681	3.181	7.5	0.755	8.255
3	0.71	3.71	8	0.756	7.756
3.5	0.725	4.225	8.5	0.757	9.257
4	0.736	4.736	9	0.758	9.758
4.5	0.744	5.244	9.5	0.759	9.259
5	0.747	5.777	10	0.76	10.76

Table V. Values of $\alpha_\pm$ and m_{HCl} when μ has various values.

No common ion present.

μ	0.01	0.0225	0.04
$m_{HCl} (10^{-3})$		$\alpha_\pm (10^{-3})$	
1	0.95	0.92	0.9
2	1.87	1.81	1.75
3	2.78	2.68	2158
4	3.73	3158	3.44
5	4.62	4.45	4.25
6	5.55	5.32	5.08
7	6.48	6.21	5.96
8	7.34	7.07	6.82
19		7.98	
10		8.83	

Fig. 4.

Fig. 5.

Qt

8×10^{-3} 7   6   5   4   3   2   1   0

0   1   2   3   4   5   6   7   8   9   10   11 12×10^{-3}

m_{HCl}

M

0.0400
0.0225
0.0100
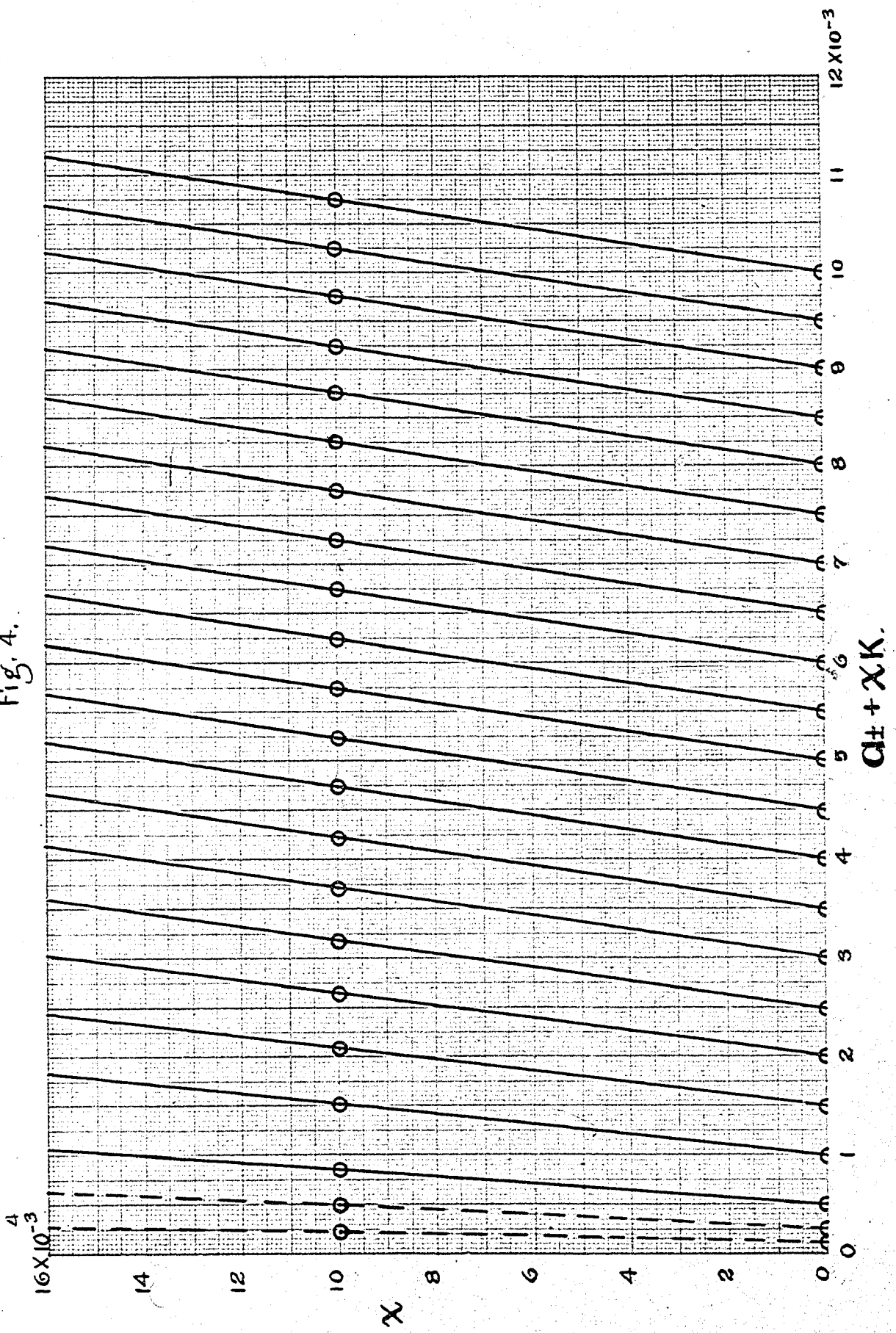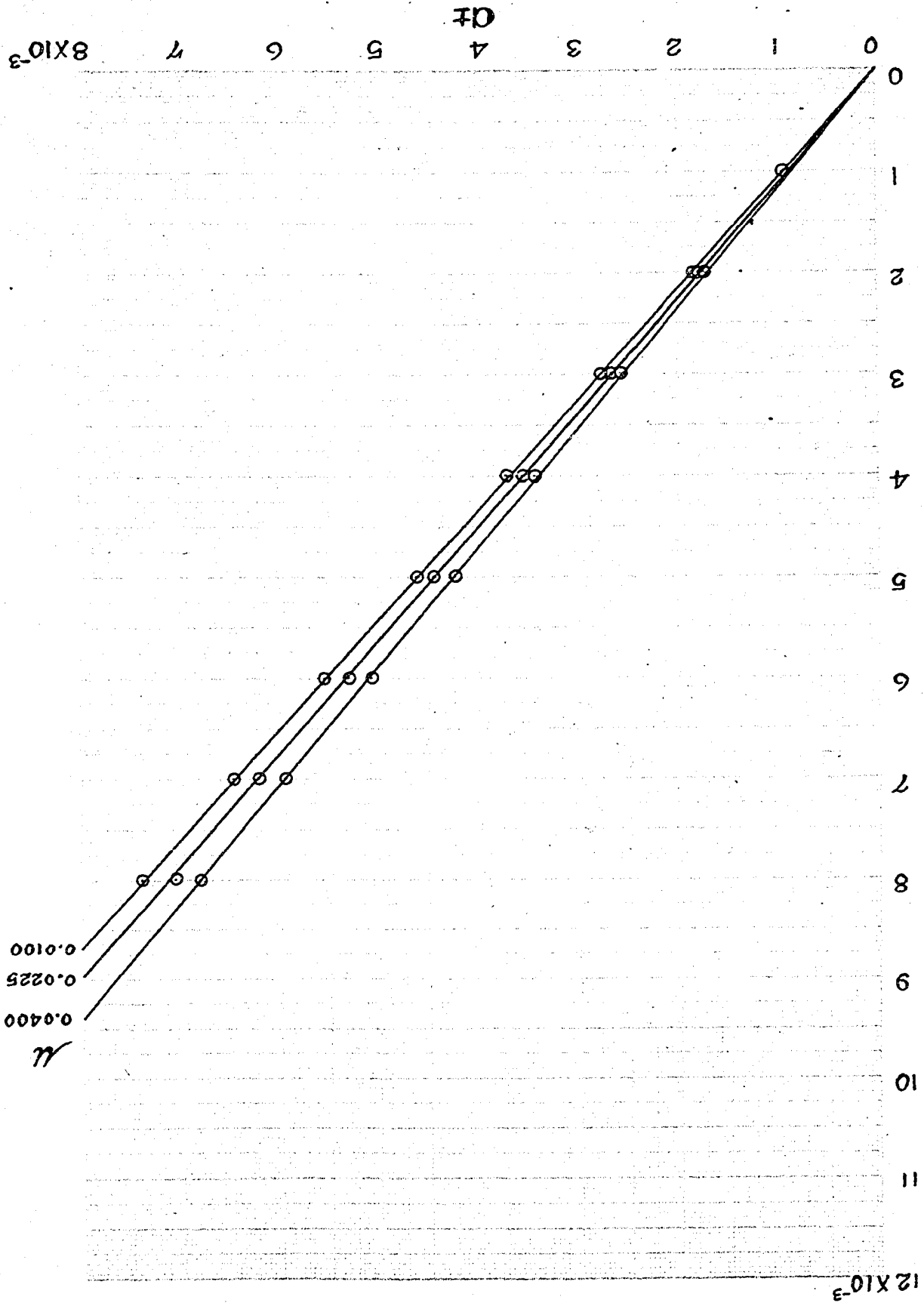
Table VI. Corresponding Values of m_{HCl} and m_2 at Various Values of $\alpha_\pm$. Common Ion Present.

$\alpha_\pm$	μ	γ	$m_{HCl}\,(10^{-5})$	$m_2\,(10^{-3})$
0.000496	0.05	0.9825	10.19	2.3981
	0.075	0.9741	4.609	5.57891
	0.1	0.9657	2.638	9.97362
	0.125	0.9572	1.718	15.60782
	0.15	0.9488	1.214	22.48786
	0.175	0.9405	0.9081	30.62491
	0.2	0.9317	0.7985	40
	0.225	0.9232	0.5702	50.625
	0.25	0.9147	0.4705	62.5
	0.275	0.9062	0.3961	75.625
	0.3	0.8976	0.3393	90

Table VII.

$\alpha_\pm$	μ	γ	$m_{HCl}\,(10^{-5})$	$m_2\,(10^{-3})$
0.000984	0.05	0.9742	40.81	2.0919
	0.075	0.9615	18.62	5.4388
	0.1	0.9491	10.75	9.8925
	0.125	0.9464	7.067	15.5443
	0.15	0.9237	5.055	22.4494
	0.175	0.9112	3.808	30.5869
	0.2	0.8982	3	40
	0.225	0.8852	2.441	50.625
	0.25	0.8727	2.034	62.5
	0.275	0.8597	1.732	75.625
	0.3	0.8470	1.499	90

Table VIII.

$\alpha_\pm$	μ	γ	$m_{HCl}\,(10^{-5})$	$m_2\,(10^{-3})$
0.001942	0.05	0.9675	161.16	0.8884
	0.075	0.9512	74.103	4.8839

	0.125	0.9464	7.067	15.5443
	0.15	0.9237	5.055	22.4494
	0.175	0.9112	3.808	30.5869
	0.2	0.8982	3	40
	0.225	0.8852	2.441	50.625
	0.25	0.8727	2.034	62.5
	0.275	0.8597	1.732	75.625
	0.3	0.8470	1.499	90

Table VIII.

0.001942	0.05	0.9675	161.16	0.8884
	0.075	0.9512	74.103	4.8839
	0.1	0.935	43.14	9.5685
	0.125	0.919	28.58	15.3392
	0.15	0.9025	20.58	22.2942
	0.175	0.886	15.69	29.4681
	0.2	0.87	12.45	39.8755
	0.225	0.853	10.24	50.5226
	0.25	0.837	8.61	62.4139
	0.275	0.821	7.398	75.5510

Table IX.

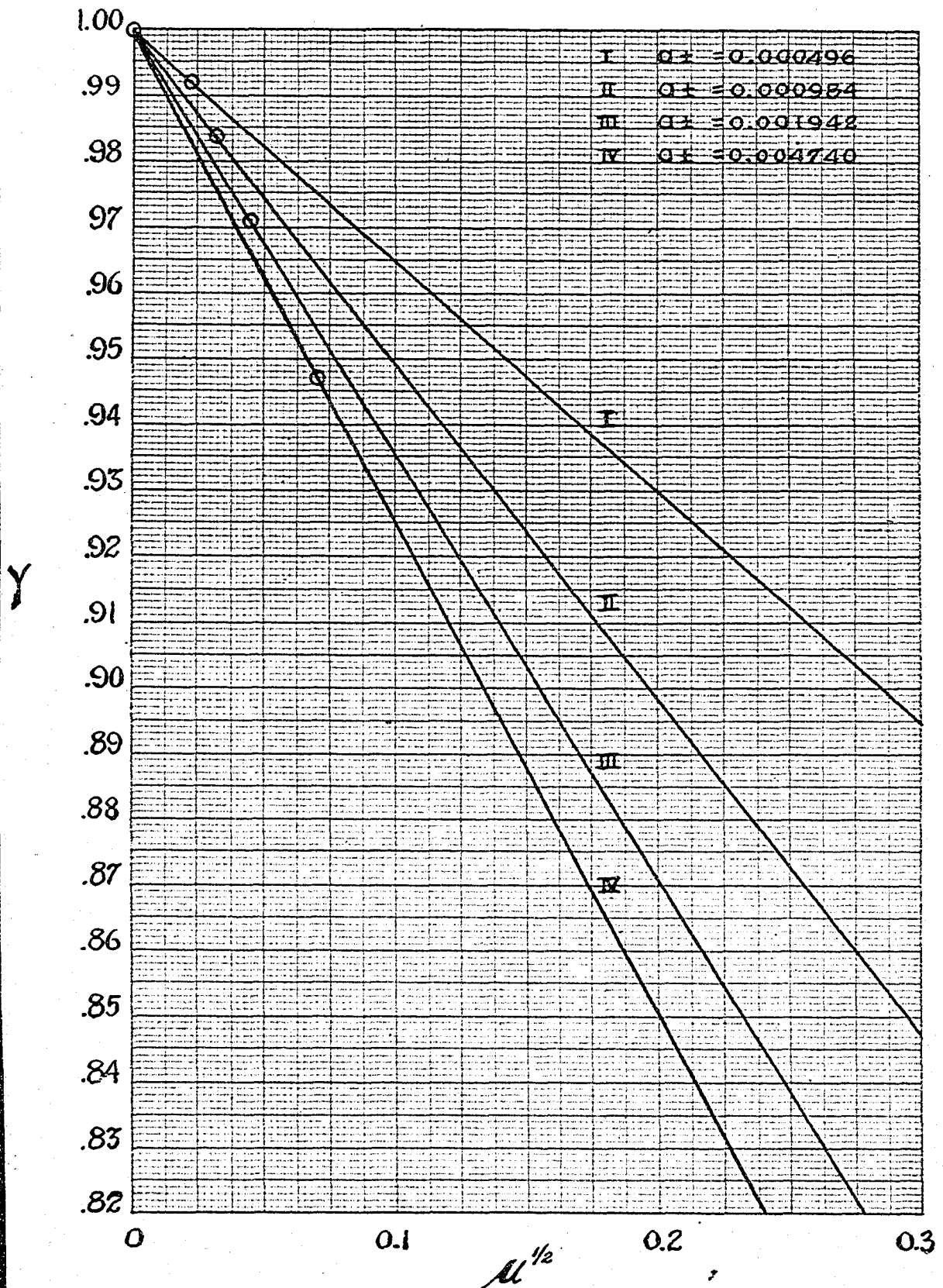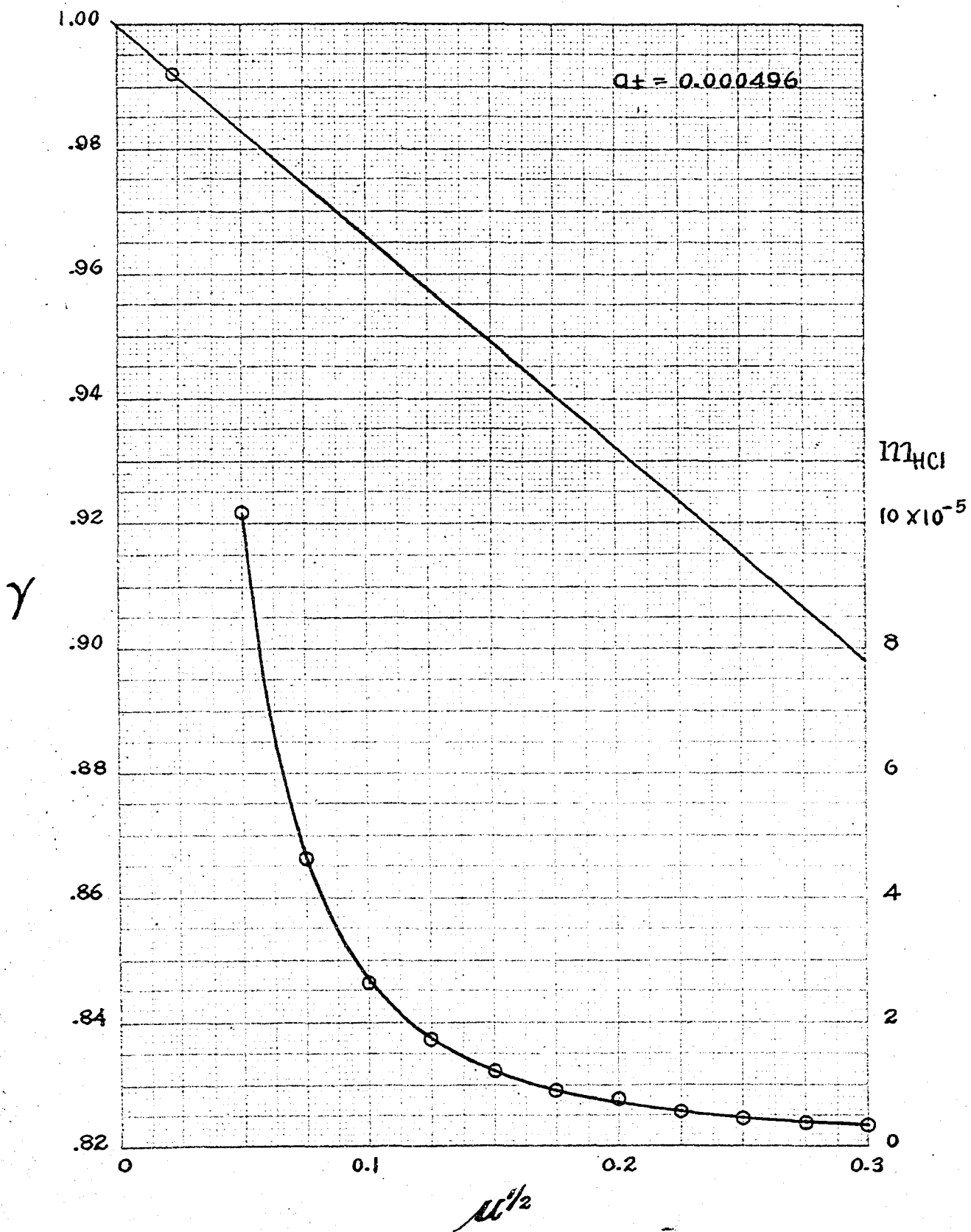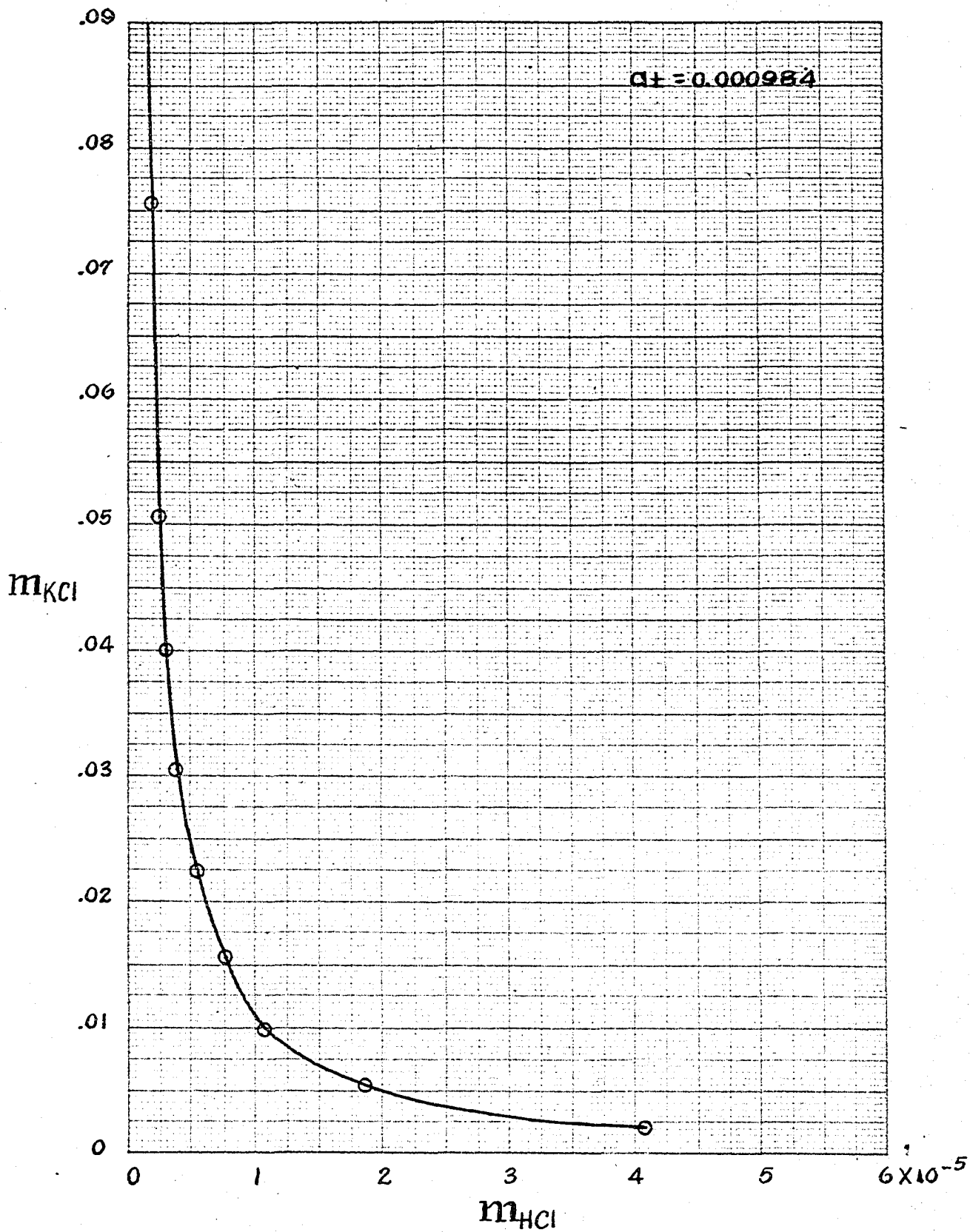|				
0.00474	0.075	0.9435	448.7	1.113
	0.1	0.9253	262.42	7.3758
	0.125	0.9066	174.95	13.8755
	0.15	0.888	126.63	21.2337
	0.175	0.8694	93.838	29.6566
	0.2	0.8505	77.651	39.2235
	0.225	0.8315	64.190	49.9831

Fig. 5A.

Fig. 6.

Fig. 6A.

Fig. 7.

Fig. 7A.

Fig. 8.

m_{HCl}

18×10^{-5} 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

0 .01 .02 .03 .04 .05 .06 .07 .08 .09

m_{KCl}

$Q_t = 0.0001942$

Fig. 8A.

Fig. 9.

Fig. 9A.

$a_{\pm} = 0.00474$
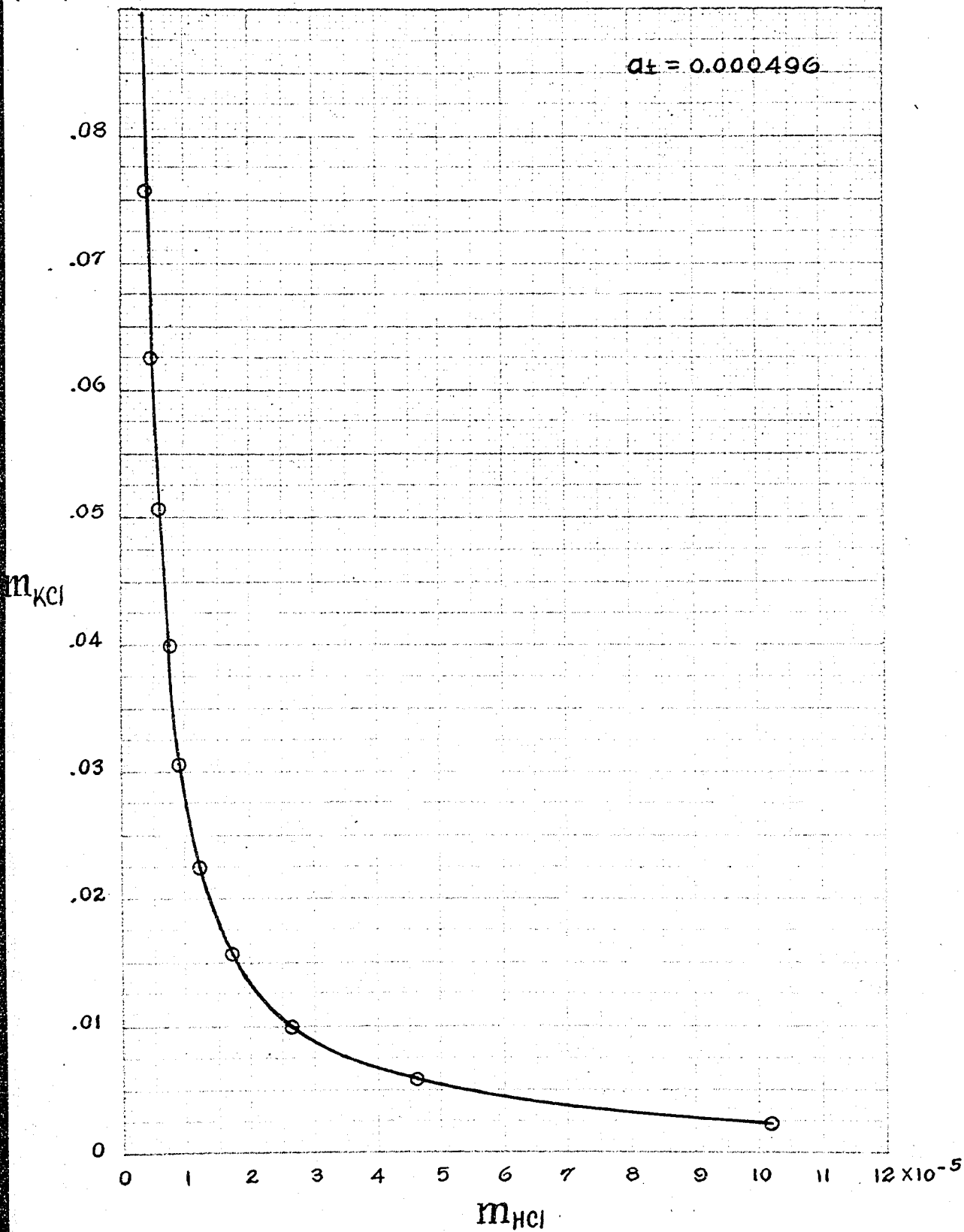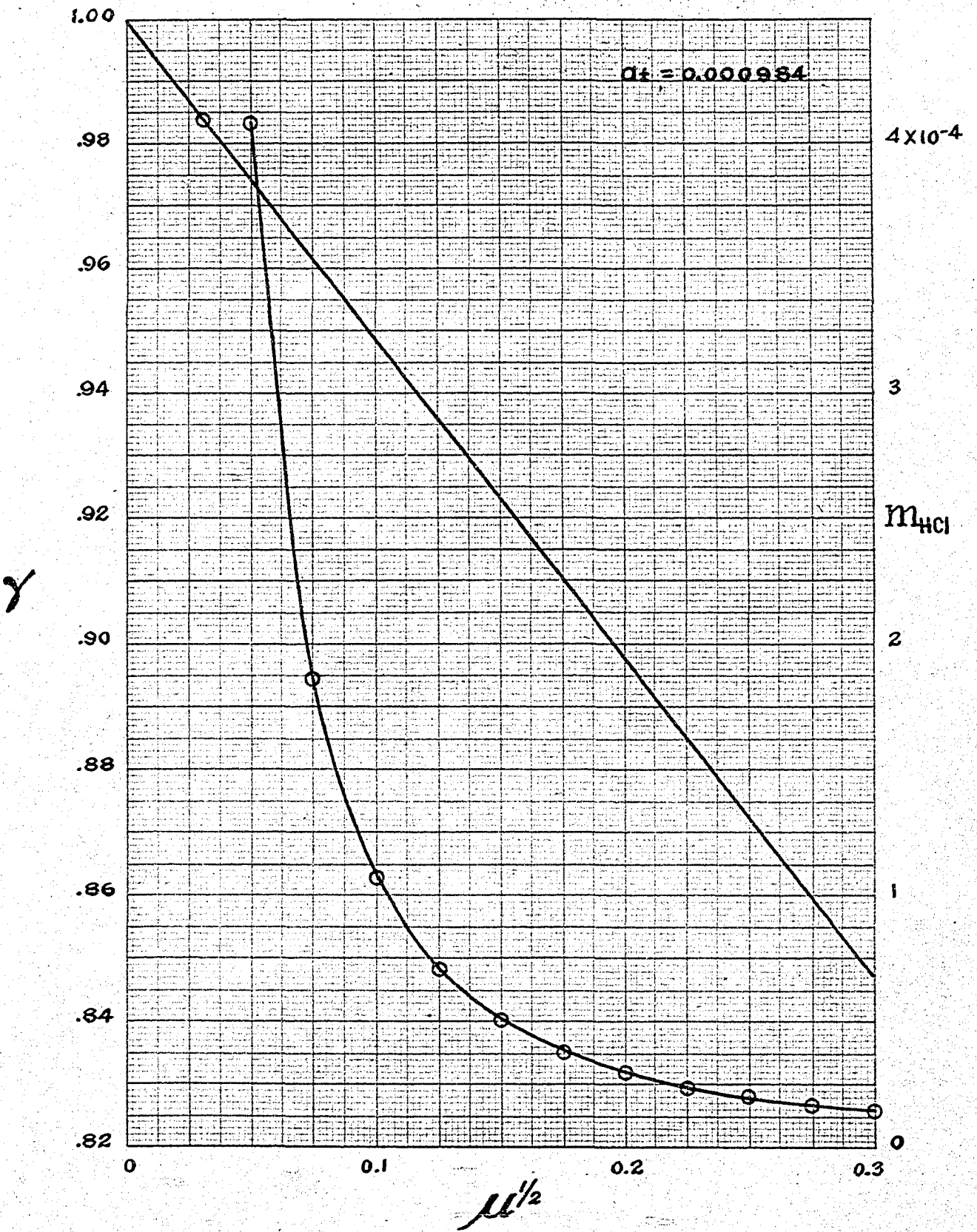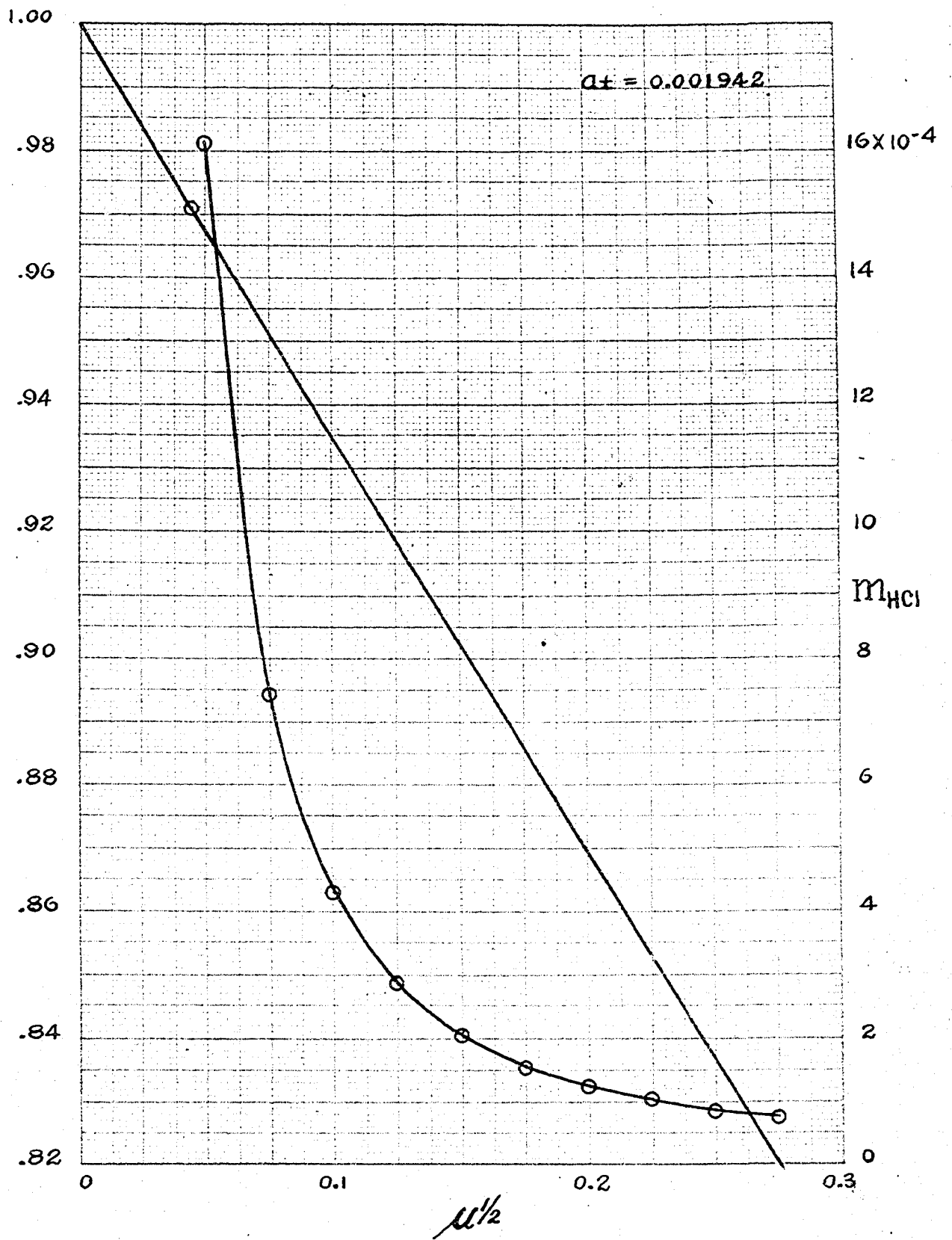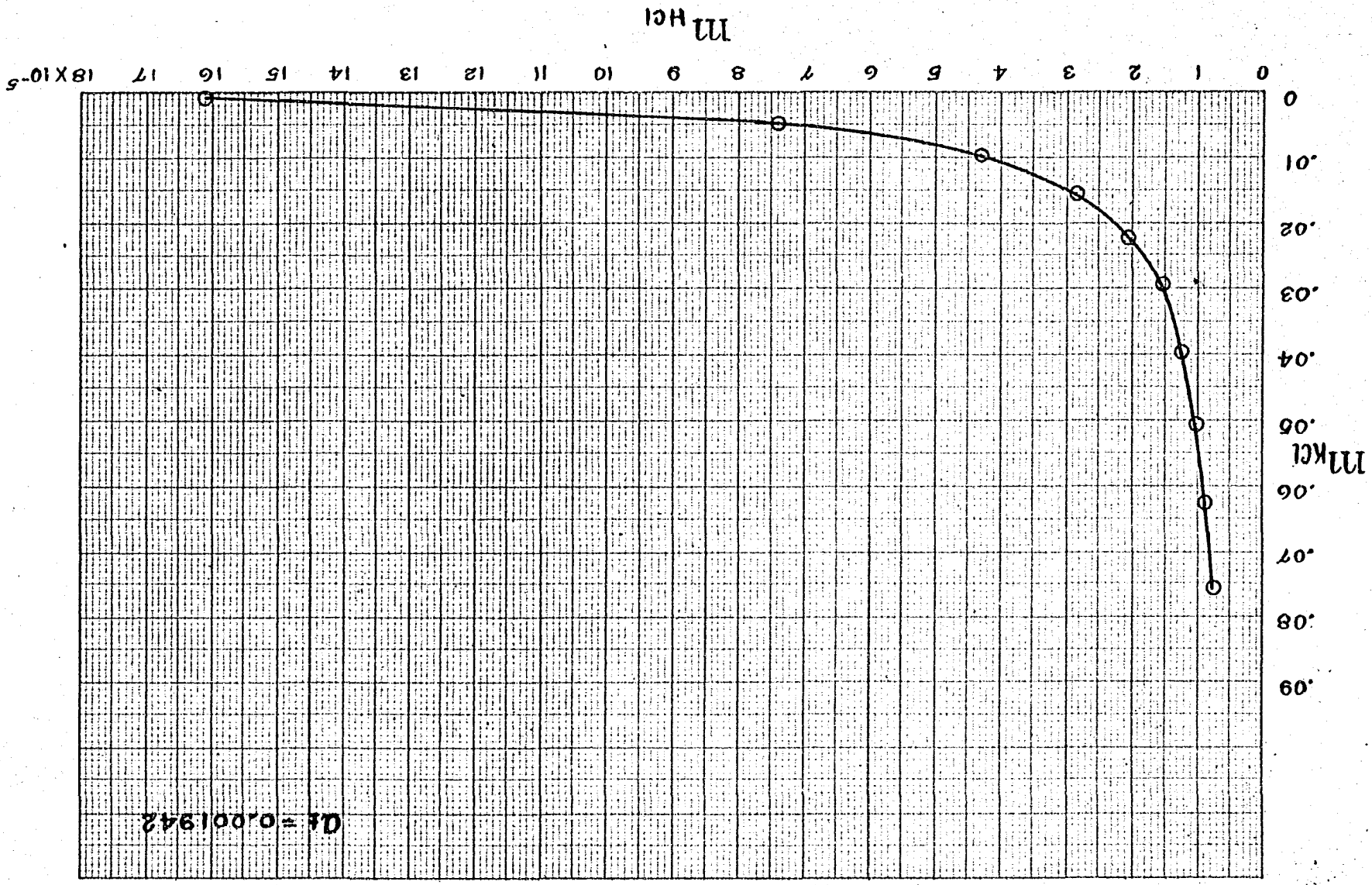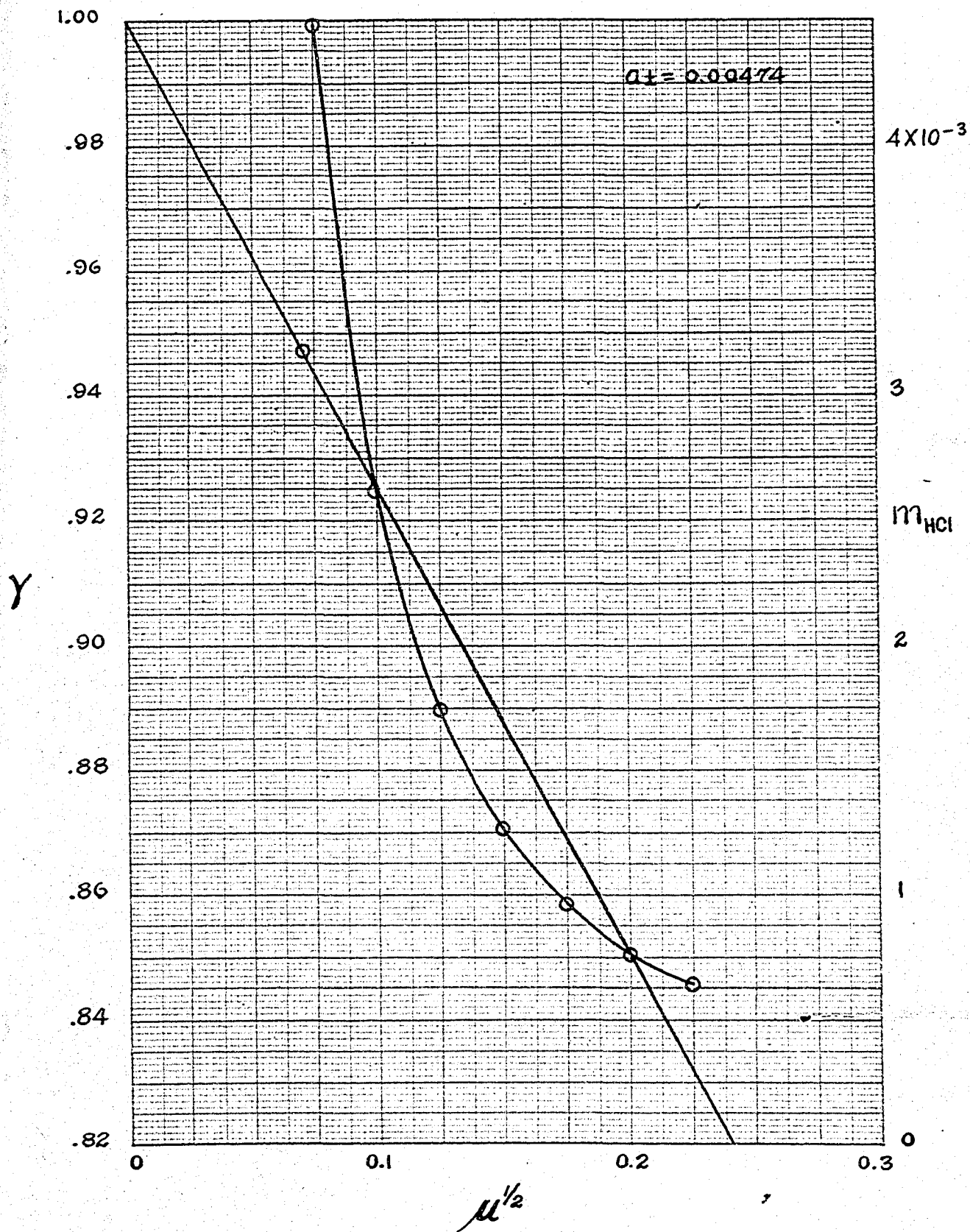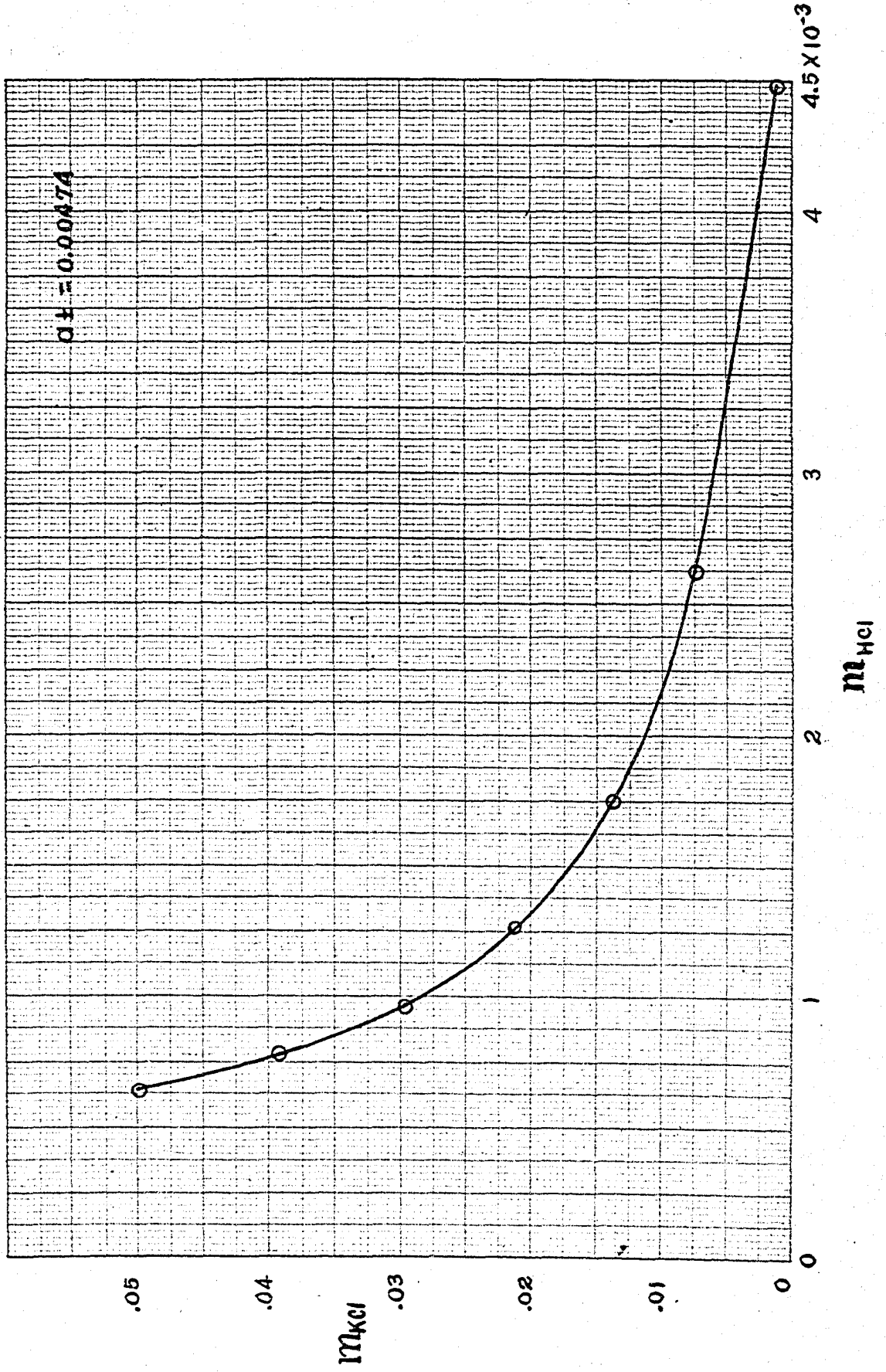
Table X. Corresponding Values of $\alpha_\pm$, α_{H^+}, m_{KCl} and $m_\pm$ at

Various Values of μ . Common Ion Present.

μ	m_{HCl}	m_{KCl}	$m_\pm (10^{-4})$	$x (10^{-5})$	$\alpha_\pm$	$\alpha_{H^+} (10^{-4})$
0.0025	0.0005	0.002	11.18	5.559	0.00107	4.83
	0.001	0.0015	1581	7.905	0.00152	9.66
	0.0015	0.001	19.37	9.685	0.00188	14.49
	0.002	0.0005	22.36	11.18	0.00215	19.32
	0.0005	0.0095	22.36	2.236	0.0021	0.46
	0.001	0.009	31.62	3.162	0.00295	0.92
	0.002	0.008	44.72	4.472	0.00414	1.84
	0.004	0.006	63.24	6.324	0.00585	3.68
	0.006	0.004	77.46	7.746	0.00709	5.52
	0.008	0.002	89.44	8.944	0.00826	7.36

Cd^{++}

24×10^{-4} 22 20 18 16 14 12 10 8 6 4 2 0

0

m_{HCl}

1

2

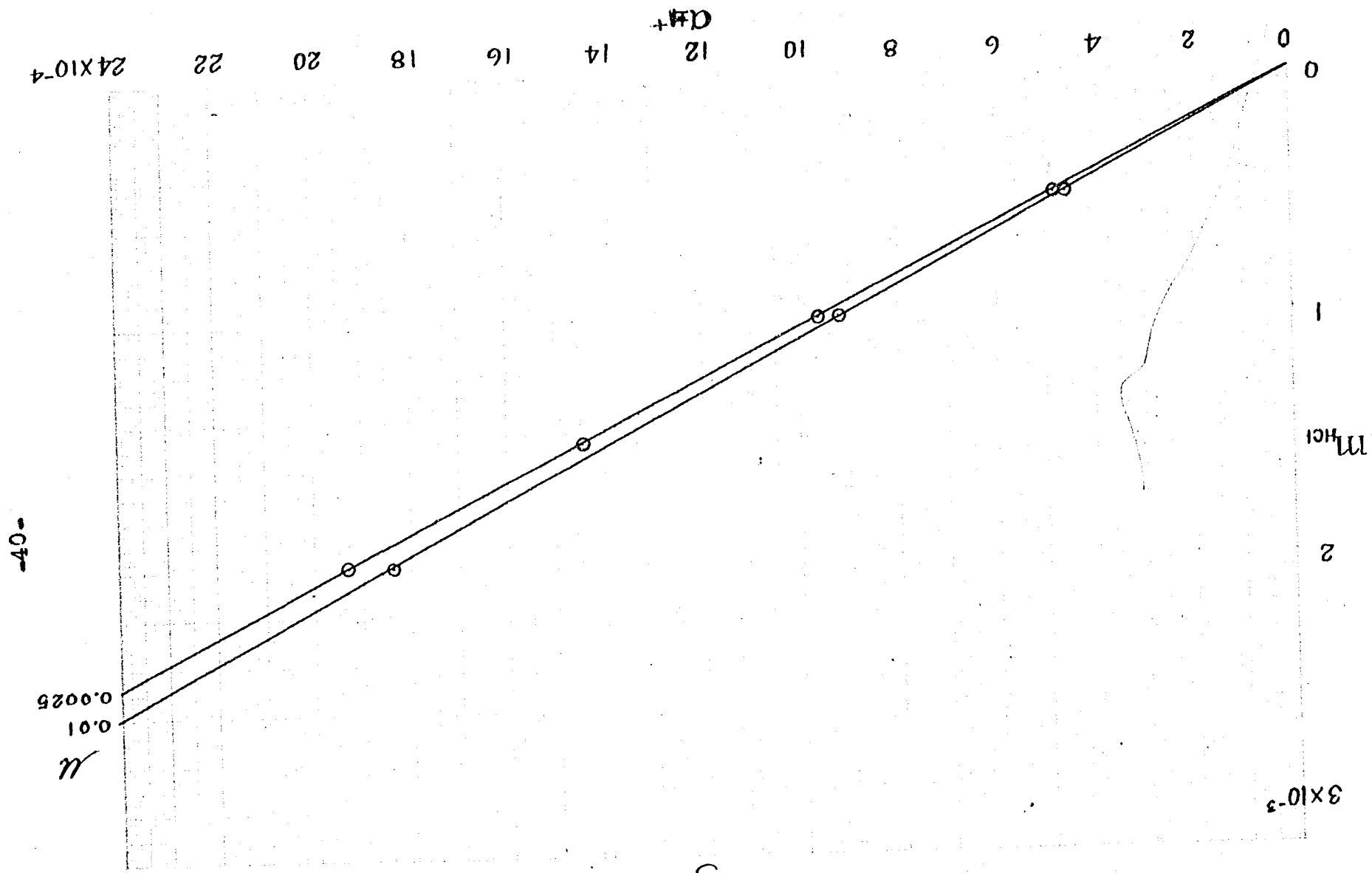3×10^{-3}

10^{-4}

0.0025
0.01

μ

Fig. 10.
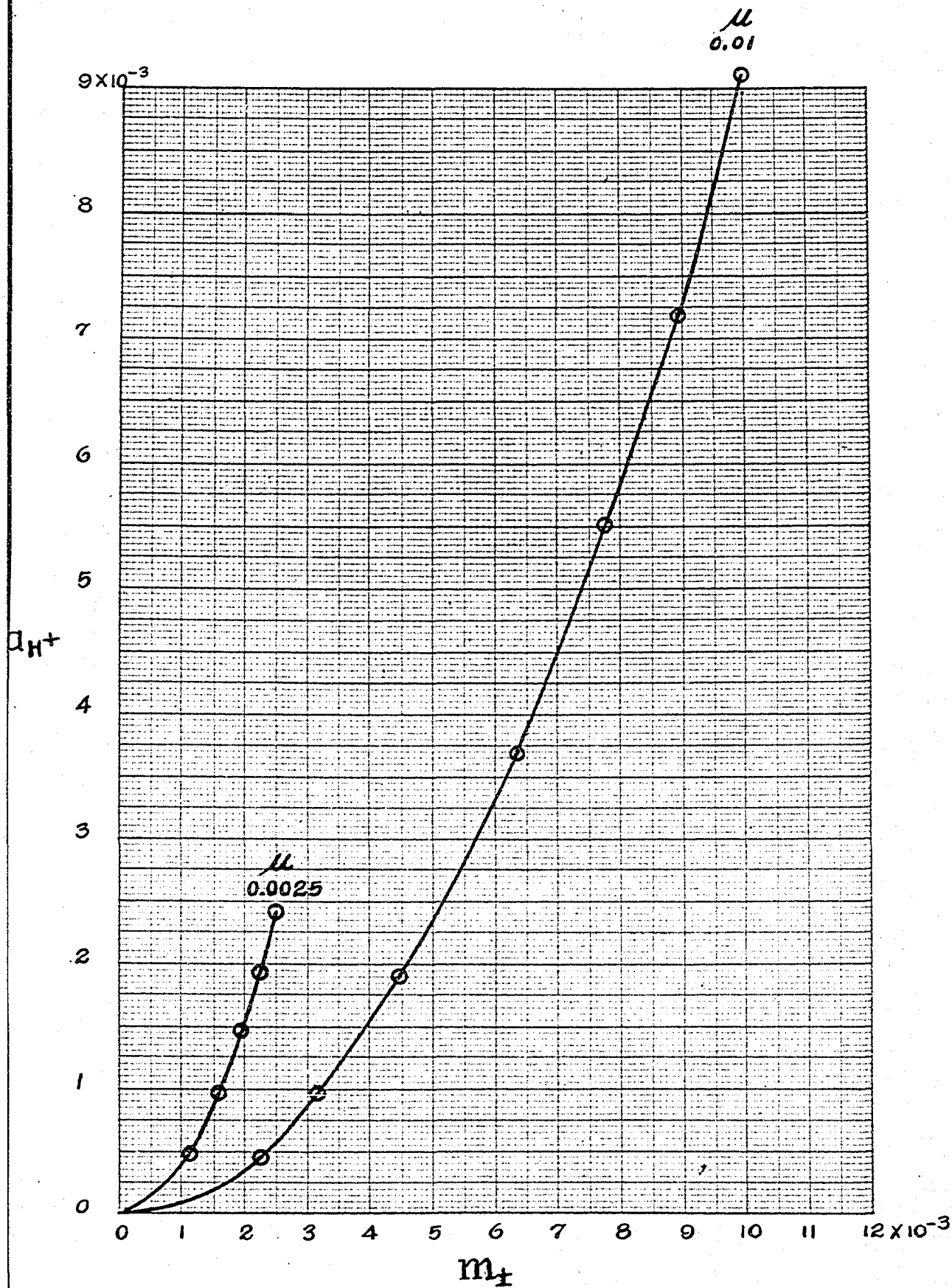
Fig. XI

LITERATURE CITED

1. G. N. Lewis, Lewis and Randall's Thermodynamics,
   McGraw-Hill Book Co., 1923.

2. Bray and Winninghoff, J. Am. Chem. Soc., 33, 1663 (1911)
   It should be stated that the concentration
   in these data is expressed in amount per
   liter and not in amount per 1000 g. of water.
   Since in dilute solutions the two methods of
   expressing concentration are essentially id-
   entical these values have not been recalcu-
   lated.

III. A PROPOSED DIAGRAM FOR THE
TERNARY SYSTEM IRON-CARBON-SILICON

The work of Charpy and Cornu Thenard[1] as well as that
of Honda and Murakami[2] indicate that the temperature of the
A_3 transition in iron is practically independent of the sil-
icon content until silicon percentages above some five to
six percent occur. Unpublished work by Ruder[3] as well as that
of Snyder, Wever and Oberhoffer[4] indicate a sharp rise in the
temperature of the A_3 transition with the first additions of
silicon. The work of these latter investigators unmistakably
indicates that the A_4 and the A_3 points are merged in pure
iron-silicon alloys at values of silicon in the neighborhood
of two percent.

The assumptions of the laws of ideal solutions within
the range properly known as dilute solutions for the solid
phases, silicon plus alpha iron and silicon plus gamma iron
in one case and for carbon plus gamma iron in the other case,
makes it possible to apply the well known equation,

$$(1) \qquad \frac{dT}{dx} = (K - 1)\frac{RT}{\Delta H}$$

where K is the distribution ratio of the solute between the
alpha and the gamma phases, e.i.,

$$K = \frac{x \text{ in alpha}}{x \text{ in gamma}}$$

K is greater than unity for silicon and is equal to zero

for carbon.

These two values of K cause equation (1) to take the following two forms:

(2) $\dfrac{dT}{dx} = M \dfrac{RT^2}{\Delta H}$

(3) $\dfrac{dT}{dx} = - \dfrac{RT^2}{\Delta H}$

where M = K-1 and is positive. Equation (2) should represent the effect of silicon on the temperature of the A_3 transition. In equation (3) K-1 = -1 since K = 0 and therefore equation (3) should represent the effect of carbon on the temperature of the A_3 transition.

If the further assumptions are made that the presence of silicon does not effect appreciably the solubility of carbon in alpha iron, and on the other hand if the presence of carbon does not effect appreciably the distribution of silicon between the alpha and the gamma phases, the general form of the solubility diagram for the ternary system iron-carbon-silicon for the temperature interval from 700°-1100° C. may be predicted from the very limited data which is now available.

This three dimensional diagram* is a modification of the earlier two dimensional diagram** and is changed so as to make it consistent with the assumption that at one percent silicon the A_3 transformation in a carbon free iron is raised to 950°C. This value is not considered as definitely established but it

* This diagram is shown on page 13.
** See Literature Citation No. 2.

is the higher of the values given by Wever and Obehoffer[4].

The same general type of modification would result if A_3 rises by either greater or smaller value than the 50°C. assumed here. The further assumption is made that at any composition to the left of the A_2 stable or A_1 metastable lines equation (2) gives the effect of silicon and equation (3) that of carbon upon the temperature of the A_3 transition.

If pressure upon the three component system iron-carbon-silicon be assumed to be constant, then the equation $P + F = 4$ gives $F = 2$ when alpha iron and solid solution are in equilibrium and when solid solution and cementite are in equilibrium. The A_3, the carbon solubility and the Acm lines become respectively the A_3, the carbon solubility and the Acm surfaces when alpha iron, carbon and solid solution are in equilibrium $F = 1$ as it does also when alpha iron, cementite and solid solution are in equilibrium. This signifies, as Kjerrman[5] has so well pointed out, that the A_1 points become A_1 lines, i.e., in this three component system, the A_1 stable and the A_1 metastable changes take place at a series of temperatures and compositions as represented by the A_1 stable and the A_1 metastable lines respectively.

In accordance with the foregoing treatment the A_3 surface is constructed from the following points:

(Si=0.00, C=0.00, T=900°C.), Si=1.00, C=0.00, T=950°C.) Wever[4]

(Si=0.00, C=0.85, T=720°C.), To a point 2°C. higher and very slightly to the left of the A_1 metastable (Si=1.00, C=0.67, T=759°C.) Hayes, Flanders and Moore.[6]

(Si=0.00, C=0.40, T=768°C.)

The Acm surface is drawn as a plane through:

(Si=0.00, C=0.85, T=720°C.) and (Si=1.00, C=0.67, T=759°C.) and in a direction to intersect Si=00, C=2.00, T=1134°C. Thus the A_1 metastable line is the intersection of the A_3 and Acm surfaces.

This manner of drawing the A_3 surface makes it distinctly curved in the zero silicon plane and makes the surface very nearly a plane at a point slightly beyond the 1.00 percent silicon plane. This was to conform to the fact that the so-called beta transformation is lowered from about 768°C. to 761°C. by the presence of this percentage of silicon.

In accordance with the method of constructing the two dimensional diagram the A_1 stable line in the three dimensional diagram is considered to be the intersection of the carbon solubility plane with the A_3 plane.

We are not as fortunate in regard to data for locating the position of the A_1 stable line in space as we were in the location of the A_1 metastable, due to the fact that the temperature and carbon content of the iron-carbon eutectoid in the pure iron carbon system are not known. The point Si=1.00,

C=0.57, T=771°C. should be very near the position of the A_1 stable line at 1.00 silicon. This point is plotted on the accompanying diagram as being slightly below and to the left of the A_3 plane. The reason that it falls off of the A_3 plane is largely due to the fact that the value for T=771°C. was determined by Hayes, Flanders and Moore [6] upon a 0.95 percent silicon alloy and the value 0.57 percent carbon was taken from the solubility studies of Schwartz, Payne, Gorton and Austin [7] which work was done upon a 1.20 percent silicon white iron.

A reasonable correction* for the variation of carbon content accompanying a variation of silicon from 1.20 percent to 0.95 percent would easily place this point upon the A_3 surface.

The general direction of the carbon solubility surface with respect to temperature and carbon is fixed by the fact that in the 1.00 percent silicon plane iron carbide is meta-

---

* NOTE--The writers wish to state that the agreement be-tween the carbon content of pearlite in a 1.00 percent sili-con white iron, as obtained by the method used in extending the A_3 line from the iron carbon eutectoid to the temperature 771°C. as shown in the paper of Hayes and Wakefield and that determined experimentally by Wakefield, is very good, indeed, if the above correction for the effect of variation of sili-con upon the carbon content of the iron carbon eutectoid is made. This does not preclude, however, the possibility of the A_3 point being raised through a considerable interval by the presence of 1.00 percent silicon as may be readily shown from the accompanying three dimensional figure.

stable and thus the carbon solubility plane lies to the left
of the Acm plane. It is also rather closely fixed by the solu-
bility studies of Schwartz, Payne, Gorton and Austin[7]. The A_1
stable line was drawn parallel to the A_1 metastable line for
want of other evidence than that of Maxwell and Hayes[8] which
shows that iron carbide is metastable at 720°C. in the pure
iron carbon system.

The behavior of a hypereutectoid alloy of about 1.00 per-
cent carbon and 0.5 percent silicon when cooled slowly from a
temperature above the critical range will be as follows: At
the point where the 0.5 silicon, 1.00 carbon vertical line
strikes the carbon solubility plane (see figure) temper carbon
begins to separate. Since the separation of carbon will not
greatly change the silicon content of the solid solution, the
composition temperature values of the solid solution will fol-
low the carbon solubility plane and will strike the A_1 stable
line at a point very near the 0.5 percent silicon point. From
this point the separation of alpha iron will cause a reduction
in the silicon content of the solid solution and this effect
will be combined with that of the separation of carbon in such
a manner as to cause the solid solution composition and temp-
erature to follow the A_1 stable line in the direction of more
carbon, less silicon and a lower temperature.

The behavior of a hypoeutectoid alloy upon cooling slow-
ly from a temperature above the critical range and containing,

for example, 0.5 percent silicon and 0.25 carbon would be as follows: At the point where the 0.5 silicon, 0.25 carbon vertical line intersects the A_3 surface (see diagram), alpha iron begins separating from the solid solution. The composition and temperature of the solid solution then follows the A_3 surface until the A_1 stable line is reached. Due to the fact that we have, in this discussion, assumed that silicon is more soluble in alpha iron than in gamma, the silicon content of the solid solution will be less than 0.5 percent when the A_1 stable line is reached as shown in the figure.

From this point of intersection, if cooling is sufficiently slow, the composition of the solid solution and its temperature follows for a limited distance the A_1 stable line in the direction of lower temperature, more carbon and less silicon. This is because the alpha iron separating along the iron-carbon eutectoid line is reducing the silicon content of the solid solution. If the rate of cooling is too rapid in the case of either the hyper or hypoeutectoid alloy, the composition of the solid solution may reach the A_1 metastable line in which case the separation of alpha iron and iron carbide will take place in such a manner as to cause the compositions and temperature of the solid solution to follow the A_1 metastable line in the direction of less silicon, more carbon and a lower temperature. In case the cooling from the higher temperature is al-

so sufficiently rapid, the Acm plane may be intersected in which case proeutectoid cementite will separate. This contingency is also shown in the figure.

The behavior accompanying the foregoing figure and discussion is the result of the writer's belief that austenite is essentially of the same fundamental nature whether it is formed from carbon or from iron carbide. Thus we may quote from a discussion of the paper of Hayes and Wakefield[9] by changing the words line to surface and point to line, as follows. First, the fact that carbon may be taken into solid solution in austenite and precipitated from the solution as cementite and the reverse process that cementite may be taken into solution and the carbon may be precipitated, indicates that there must be a mechanism for the conversion of carbon in each of these forms into the other. If such is the case, the solid solution is very probably the same in both cases. If we accept the concept of the solid solution as that which Wever presents and which reference Mr. Schwartz[7] quotes, we may conclude that the carbon in the austenite enters the interior of the face-centered cube whether it comes from carbon or from cementite and that the iron atoms in the cementite take their place in the regular positions of the iron in these face-centered cubes. If this is correct, the cementite is formed at the time that the carbon is precipitated. At the iron-carbon eu-

tectoid carbon is precipitated without the formation of the
carbide. This being the case, it follows that the difference
between austenite saturated with carbon from carbon and satur-
ated with carbon from cementite is simply that a greater num-
ber of the face-centered cubes in the solution saturated with
carbon from cementite have their interior occupied by a carbon
atom. This concept at least conforms to our present knowledge
of the structure of austenite as derived from X-ray studies.

One of the writers has stated elsewhere that this same
statement can be made of austenite in the presence of more than
one form of the solute (dissolved carbon) if such forms are in
equilibrium with each other.

In either of the above contingencies, alpha iron should
separate where the carbon solubility plane crosses the A_3 sur-
face. For equilibrium processes there should be no discon-
tinuity in the A_3 surface.

If these conclusions are correct, it becomes evident that
there is only on A_3 surface. This being the case there is only
one A_3 point in the pure iron-carbon system and it is the sta-
ble A_3 and occurs at about $900^\circ C$. Certainly there is no sig-
nificance to the A_3 transition in pure iron except that it re-
presents a stable transition for the phase gamma iron is a
stable phase above its temperature and the alpha phase is a
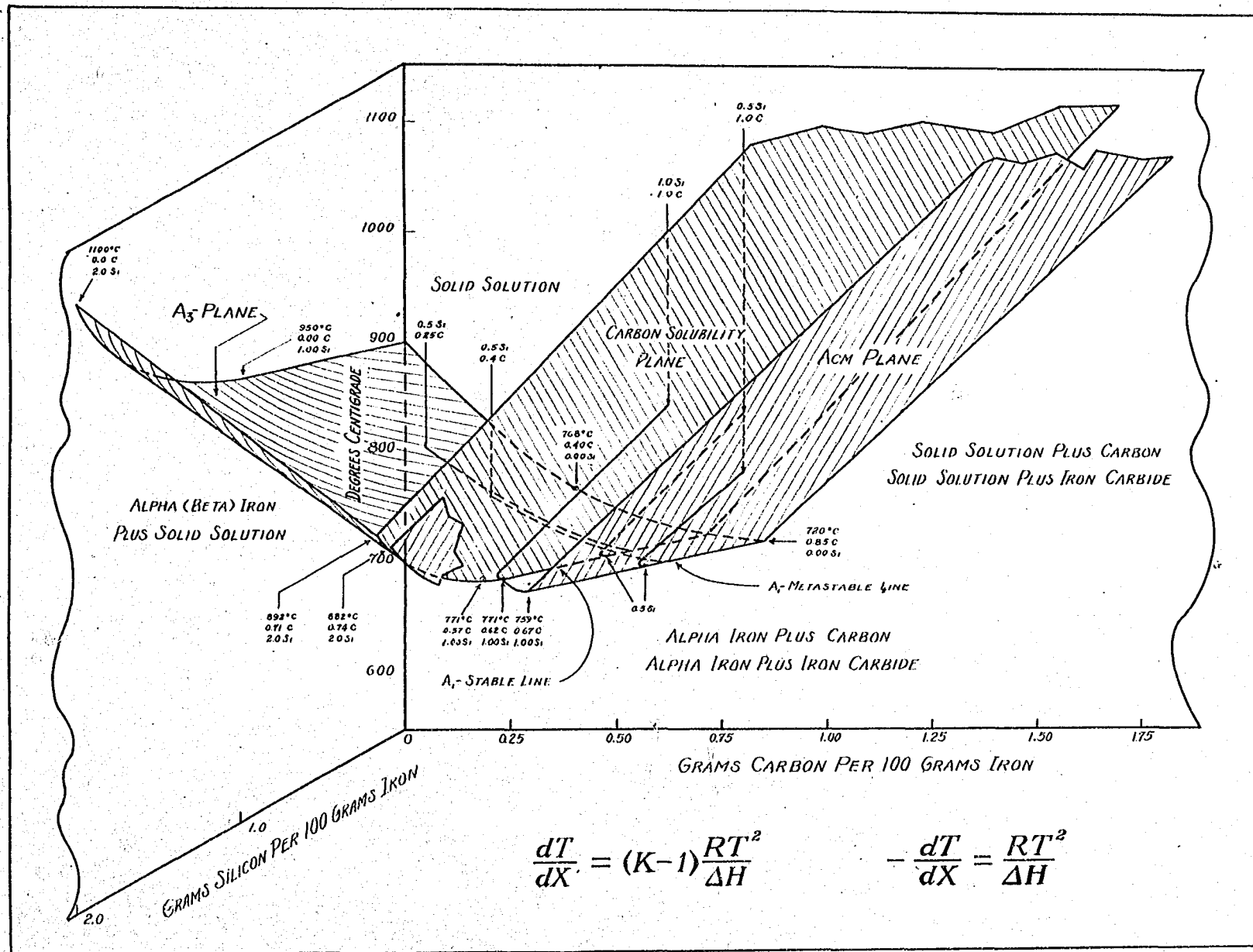stable phase below it.

There is another fact which seems to the writers to be a fundamental objection to a value for A_3 stable at any other temperature than the one which is usually taken (900°C.). Suppose we assume that there are two molecular weights of the solute, one which we will call (C) and the other (Fe_3C). For dilute solutions the slope of the A_3 line is given by equation (2) and under such circumstances it may be integrated to the form $\Delta T = \frac{RT^2}{\Delta H} X$ where X is the mole fraction of either the (C) (Fe_3C) as the case may be. Now in the iron-carbon diagram the abscissa is percent carbon and at low values for carbon the value for X, if we assume (C) to be the solute, is very nearly the same as the value for X if we assume (Fe_3C) as the solute. The fact is that the values of X would not differ by more than 4 percent even up to 0.5 percent carbon. As zero carbon is approached they approach each other and at zero carbon become identical. Hence it appears that there would be only the one A_3-point at zero carbon and silicon even if it be granted that two absolutely independent solid solutions may exist. The The writers, therefore, doubt the existence of an A_3 stable transition either in pure iron carbon alloys or in iron carbon silicon alloys containing not more than one or two percent silicon.

The writers regret that there is not more dependable data from which the three dimensional diagram might be extended, for

example, a few more points for the A_3, A_1 stable and A_1 metastable would be of great assistance in determining the manner in which these three change in curvature. It is of interest to note that according to Wever, with silicon contents between one percent and two percent, the temperature of the A_3 transition in pure iron-silicon alloys rises very rapidly. This makes the A_3 surface distinctly concave upward. Now if the Acm surface and the carbon solubility surface should remain nearly plane or should become concave downward, the A_1 stable and A_3 metastable lines would both be turned upward and toward the right, that is, in the direction of less rapidly decreasing carbon contents and later to increasing carbon contents. If this represents the behavior, it is evident that neither the carbon content of A_1 stable or A_1 metastable would become zero, and also it is evident that their temperature would rise possibly above 1000*C with higher silicon contents.

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1100

1000

900

800

700

600

1100°C
0.0 C
2.0 Si

A₃ PLANE

950°C
0.00 C
1.00 Si

SOLID SOLUTION

0.5 Si
0.25 C

0.5 Si
0.4 C

0.5 Si
1.0 C

1.0 Si
.10 C

CARBON SOLUBILITY
PLANE

ACM PLANE

768°C
0.10 C
0.00 Si

SOLID SOLUTION PLUS CARBON

SOLID SOLUTION PLUS IRON CARBIDE

DEGREES CENTIGRADE

ALPHA (BETA) IRON

PLUS SOLID SOLUTION

720°C
0.85 C
0.00 Si

A₁ METASTABLE LINE

892°C
0.71 C
2.0 Si

682°C
0.74 C
2.0 Si

771°C
0.57 C
1.0 Si

771°C
0.42 C
1.00 Si

759°C
0.67 C
1.00 Si

0.5 Si

ALPHA IRON PLUS CARBON

ALPHA IRON PLUS IRON CARBIDE

A₁ STABLE LINE

0   0.25   0.50   0.75   1.00   1.25   1.50   1.75

GRAMS CARBON PER 100 GRAMS IRON

1.0

GRAMS SILICON PER 100 GRAMS IRON

2.0

$$\frac{dT}{dX} = (K-1)\frac{RT^2}{\Delta H} \qquad -\frac{dT}{dX} = \frac{RT^2}{\Delta H}$$