Absorption of Diatomic Gas by Binary Alloys. I

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Synopsis

Experimental results formerly reported on the absorption of nitrogen gas by molten binary alloys were considered from the viewpoint of statistical thermodynamics.

According to the former results, gas atoms α dissolved in the interlattice positions in quasi-crystal of molten alloy lattice are not distributed uniformly and the distribution depends upon the amount of interaction energies $\mathscr{P}_{B\alpha}$ and $\mathscr{P}_{A\alpha}$ of α-atom with metal atoms A and B; that is, nitrogen atoms have a tendency to cluster around chromium or manganese atoms when nitrogen is absorbed by molten Fe-Cr or Fe-Mn alloys.

Taking the above-mentioned fact into account, the theoretical formula concerning the absorption of diatomic gas by binary alloys was derived.

It could explain satisfactorily the results formerly obtained with respect to nitrogen absorption by molten Fe-Cr, Fe-Mn and Fe-Ni alloys.

Further, the validity of the present theory was checked by some previous data on the absorption of diatomic gases (nitrogen, hydrogen or oxygen) by binary solid solutions.

I. Introduction

In the previous reports,[1] the author investigated experimentally the absorption phenomena of nitrogen by molten iron alloys and some considerations were given on the results from the stand-point of statistical thermodynamics.

On the following conceptions obtained from the former reports, the theory in this report were constructed :

    i)   metals and alloys have quasi-crystalline structure in molten state ;

    ii) such diatomic gases as nitrogen, hydrogen and oxygen dissolve interstitially in the quasi-crystalline lattice of molten metals and alloys ;

    iii) these dissolved gas atoms are distributed uniformly (statistically) in the interlattice positions of pure metals ;

iv) but, when gas atoms α dissolve in the alloy lattice AB, they are not generally distributed uniformly in the interlattice positions, and the distribution depends upon the amount of interaction energies $\varphi_{A\alpha}$ and $\varphi_{B\alpha}$ (the interaction energies between A-α atoms and B-α atoms, respectively) ; that is, in the case of absorption of nitrogen by Fe-Cr alloys, nitrogen atoms which have greater affinity to chromium atom than to iron atom have a tendency to cluster around chromium atoms.

Taking the above mentioned facts into account, the general theoretical formulas were derived concerning the absorption of diatomic gas by binary alloys which are poor absorber.*

II. Theoretical consideration

A) General representation of distribution of atoms in the quasi-crystal of · molten metals

Let us consider a binary alloy AB as consisting of N_A atoms of A and N_B atoms of B in which N_α atoms of α are dissolved interstitially. Then, the total number N' of possible sites of α is equal to the total number N of metal atoms ; i. e., $N' = N$, $N_A + N_B = N$ and $N_0 + N_\alpha = N'$, where N_0 is the number of unoccupied sites of α.

When we denote by $\eta_\alpha^A \equiv \eta$ the probability of occurence of α-atoms around A-atom, by η_0^A that of unoccupied sites of α around A-atom and by ζ_B^A that of B-atoms around A-atom, etc., then a certain distribution of atoms of A, B and α can generally be expressed by (1) as a function of η :

$$
\left.
\begin{aligned}
&\eta_\alpha^A \equiv \eta, \quad \eta_0^A = 1 - \eta, \quad \eta_A^\alpha = N_A \eta / N_\alpha, \quad \eta_0^\alpha = 1 - \eta_A^\alpha = (N_\alpha - N_A \eta)/N_\alpha, \\
&\eta_A^0 = N_A(1-\eta)/N_0, \quad \eta_B^0 = (N_0 - N_A + N_A \eta)/N_0 = (N_B - N_\alpha + N_A \eta)/N_0, \\
&\eta_\alpha^B = (N_\alpha - N_A \eta)/N_B, \quad \eta_0^B = (N_B - N_\alpha + N_A \eta)/N_B, \\
&\zeta_B^A = \eta \, \eta_B^\alpha + \eta_0^A \, \eta_B^0 = \eta(N_\alpha - N_A \eta)/N_\alpha + (1-\eta)(N_B - N_\alpha + N_A \eta)/N_0, \\
&\zeta_\alpha^\alpha = \eta_A^\alpha \, \eta_\alpha^A + \eta_B^\alpha \, \eta_\alpha^B = N_A \eta^2 / N_\alpha + (N_\alpha - N_A \eta)^2 / N_\alpha N_B.
\end{aligned}
\right\} \quad (1)
$$

If there is a considerable difference between $\varphi_{A\alpha}$ and $\varphi_{B\alpha}$, namely, the interaction energies of the pairs of A-α atoms and B-α atoms, respectively, the distribution of atoms A, B and α can generally be expressed by (1), and in the special case when $\varphi_{A\alpha} = \varphi_{B\alpha}$, the uniform distribution of A, B and α atoms takes place, that is,

$$
\eta = N_\alpha / N, \quad \eta_0^A = (N - N_\alpha)/N, \quad \eta_A^\alpha = N_A/N, \cdots\cdots\cdots .
$$

B) Energy of the atom assembly ·

The energy W of such an atom group as expressed by (1) can also be expressed by (2) as a function of η :

$$W = \tfrac{1}{2} N_A z \zeta_A^A \varphi_{AA} + \tfrac{1}{2} N^B z \zeta_B^B \varphi_{BB} + N_A z \zeta_B^A \varphi_{AB}$$
$$+ N_A z' \eta \varphi_{A\alpha} + N_B z' \eta_\alpha^B \varphi_{B\alpha} + \tfrac{1}{2} N_\alpha z \zeta_\alpha^\alpha \varphi_{\alpha\alpha} \qquad\qquad\Big\} \quad (2)$$
$$= \tfrac{1}{2}(N_A \Psi_A + N_B \Psi_B) + \tfrac{1}{2} N_A \zeta_B^A \Psi_1 + N_A \eta \Psi_{A\alpha} + N_B \eta_\alpha^B \Psi_{B\alpha} + \tfrac{1}{2} N_\alpha \zeta_\alpha^\alpha \Psi_{\alpha\alpha}.$$

In expression (2) we write $z\varphi_{AA} \equiv \Psi_A$, $z\varphi_{BB} \equiv \Psi_B$, $z'\varphi_{A\alpha} \equiv \Psi_{A\alpha}$, $\Psi_1 \equiv 2\Psi_{AB} - (\Psi_A + \Psi_B)$, for brevity; z is the number of nearest neighbouring atoms around a metal atom, and z' that around a α-atom, i. e., $z = 12$, $z' = 6$ in the solid crystal of face-centered cubic lattice and $z \doteqdot 12$, $z' \doteqdot 6$ in molten metal.

When we consider a poor absorber in which $\Psi_{AB} \doteqdot (\Psi_A + \Psi_B)/2$, i. e., $\Psi_1 \doteqdot 0$, then equation (2) can be replaced by equation (3),

$$W \doteqdot \tfrac{1}{2}(N_A \Psi_A + N_B \Psi_B) + N_A \eta \Delta \Psi_\alpha + N_\alpha \Psi_{B\alpha}, \quad\ldots\ldots\ldots\ldots(3)$$

where $\Delta\Psi_\alpha \equiv \Psi_{A\alpha} - \Psi_{B\alpha}$.

In the case of good absorber, $\Psi_{\alpha\alpha}$ should not be neglected. With respect to such a good absorber, detailed considerations will be given in the near future.

C) Derivation of absorption formula from the thermodynamical functions

Free energy G^m of the atomic group expressed by (1) can be given by the following equation (4), in which Γ^m is the partition function :

$$G^m = -kT \ln \Gamma^m = -kT \ln [G(\eta) e^{-W/kT} (J_A)^{N_A} (J_B)^{N_B} (J_\alpha)^{N_\alpha}] \Big\}$$
$$= -kT \ln G(\eta) + W - kT(N_A \ln J_A + N_B \ln J_B + N_\alpha \ln J_\alpha). \quad\Big\} \quad (4)$$

In the equation (4), $G(\eta)$ is the number of complexion of the atom assembly which is determined by N_A, N_B and η ; J_A, J_B and J_α are the vibrational partition functions of A, B and α atoms, respectively.

a) Calculation of the complexion number $G(\eta)$

$G(\eta)$ is the number of ways of distributing N_A atoms of A and N_B atoms of B over the N lattice sites and N_α atoms of α over N' interlattice sites. $G(\eta)$ should also satisfy the relation of (1). The method of calculating the functional form of such a function as $G(\eta)$ was already reported by Fowler, Guggenheim[2] and Takeuchi.[3] Therefore, it will be briefly described here.

Let us denote by $w(\eta)$ the number of pairs which satisfy the relation (1), then

$$w(\eta) = \frac{(z'N')!}{(N_\alpha z' \eta_A^\alpha)! \, (N_\alpha z' \eta_B^\alpha)! \, (N_0 z' \eta_A^0)! \, (N_0 z' \eta_B^0)!} , \qquad (5)$$

since the total number of pairs is $z'N'$.

We can obtain an approximate value of $G(\eta)$ by introducing a normalizing

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(2) R. H. Fowler and E. A. Guggenheim, Proc. Roy. Soc., **178** (1940), 189.

(3) S. Takeuchi, Japan Inst. Metals, **5** (1941), 413.

facter h which is independent of η as

$$G(\eta) = h \cdot w(\eta). \tag{6}$$

Since the following relation holds,

$$\sum_\eta G(\eta) = \frac{N!}{N_A! N_B!} \frac{N'!}{N_\alpha! N_0!}, \tag{7}$$

we can evaluate h, at least approximately, from (6) and (7) as follows :

$$\sum_\eta G(\eta) = h \sum_\eta w(\eta) = \frac{N!}{N_A! N_B!} \frac{N'!}{N_0! N_\alpha!}. \tag{8}$$

Hence,

$$h = \frac{N!}{N_A! N_B!} \frac{N'!}{N_\alpha! N_0!} \frac{1}{\sum_\eta w(\eta)}. \tag{9}$$

Now, we can calculate $\sum_\eta w(\eta)$ in equation (9) with sufficient accuracy by identifying $\sum_\eta w(\eta)$ with its maximum term. The maximum term is determined by the condition $\partial \ln w(\eta)/\partial \eta = 0$, which gives $\eta^* = N_\alpha/N$, the value of η which corresponds to purely random arrangements of pairs of neighbouring atoms. It follows, with sufficient accuracy that,

$$
\begin{aligned}
h &= \frac{N!}{N_A! N_B!} \frac{N'!}{N_\alpha! N_0!} \frac{1}{w(\eta^*)} \\
&= \frac{N!}{N_A! N_B!} \frac{N'!}{N_\alpha! N_0!} \frac{(N_\alpha z' \eta_A^{\alpha*})! (N_\alpha z' \eta_B^{\alpha*})! (N_0 z' \eta_A^{0*})! (N_0 z' \eta_B^{0*})!}{(z' N')!}.
\end{aligned}
\tag{10}
$$

The corresponding explicit expression for $G(\eta)$ is derived from (5) and (10) as follows :

$$G(\eta) = \frac{N!}{N_A! N_B!} \frac{N'!}{N_\alpha! N_0!} \frac{(N_\alpha z' \eta_A^{\alpha*})! (N_\alpha z' \eta_B^{\alpha*})! (N_0 z' \eta_A^{0*})! (N_0 z' \eta_B^{0*})!}{(N_\alpha z' \eta_A^{\alpha})! (N_\alpha z' \eta_B^{\alpha})! (N_0 z' \eta_A^{0})! (N_0 z' \eta_B^{0})!}. \tag{11}$$

$$
\begin{aligned}
\therefore \ \ln G(\eta) = &\ N \ln N + N' \ln N' - (N_A \ln N_A + N_B \ln N_B + N_\alpha \ln N_\alpha + N_0 \ln N_0) \\
&- z' \left\{ N_A \eta \ln \frac{\eta (N_B - N_\alpha + N_A \eta)}{(1-\eta)(N_\alpha - N_A \eta)} + N_A \ln (1-\eta) + N_B \ln \frac{(N_B - N_\alpha + N_A \eta)}{N_B} \right. \\
&\left. + N_\alpha \ln \frac{(N_\alpha - N_A \eta)}{N_\alpha} - N_\alpha \ln \frac{(N_B - N_\alpha + N_A \eta)}{N} + N_0 \ln \frac{N}{N_0} \right\}.
\end{aligned}
\tag{12}
$$

By inserting (3) and (12) in (4), the free energy G^m is obtained as a function of η as follows :

$$G^m = \tfrac{1}{2}(N_A\,\Psi_A + N_B\,\Psi_B) + N_\alpha\,\Psi_{B\alpha}$$

$$- kT\left[N\ln N + N'\ln N' - N_0\ln N_0 + N_A\ln\frac{J_A}{N_A} + N_B\ln\frac{J_B}{N_B} + N_\alpha\ln\frac{J_\alpha}{N_\alpha}\right]$$

$$+ z'\,kT\left[N_A\ln(1-\eta) + N_B\ln\frac{(N_B - N_\alpha + N_A\eta)}{N_B} + N_\alpha\ln\frac{(N_\alpha - N_A\eta)}{N_\alpha}\right.$$

$$\left.- N_\alpha\ln\frac{(N_B - N_\alpha + N_A\eta)}{N} + N_0\ln\frac{N}{N_0}\right]. \tag{13}$$

It is desirable to express the free energy G^m and other thermodynamical functions as functions of $\Delta\Psi_\alpha$, since $\Delta\Psi_\alpha$ determines the distribution of atoms. For this purpose the functional form of η will be derived from the following condition of stability.

b) Functional form of η

Since the distribution expressed by equation (1) is the most stable one under the given condition, the free energy G^m of the distribution is the minimum, compared with other distributions, that is,

$$\partial G^m/\partial\eta = 0.$$

From equation (4), we have

$$\frac{\partial W}{\partial\eta} - kT\frac{\partial\ln G(\eta)}{\partial\eta} = 0. \tag{14}$$

From equations (3) and (12), equation (14) becomes

$$\Delta\Psi_\alpha + z'\,kT\ln\frac{\eta(N_B - N_\alpha + N_A\eta)}{(1-\eta)(N_\alpha - N_A\eta)} = 0. \tag{15}$$

Now, if we put

$$\kappa \equiv \frac{\eta(N_B - N_\alpha + N_A\eta)}{(1-\eta)(N_\alpha - N_A\eta)}, \tag{16}$$

equation (15) will be reduced to

$$\Delta\Psi_\alpha + z'\,kT\ln\kappa = 0 \qquad \text{or} \qquad \kappa = e^{-\Delta\Psi_\alpha/z'kT}. \tag{15'}$$

The approximate value of η is given by equation (17) as a function of $\Delta\Psi_\alpha$ (or κ) from equation (16) as

$$\eta \doteq \frac{\kappa N_\alpha}{\kappa N_A + N_B + N_\alpha(\kappa-1)}. \tag{17}$$

In this calculation η^2-term was neglected since η is small in the case of poor absorber.   For example, $\eta\doteqdot0.001,5$ for molten pure iron, according to the former experiment [1].

Furthermore, equation (17) can be reduced to equation (18) in the case of poor absorber, because N_α is negligible compared with N_A and N_B.

$$\eta \fallingdotseq \frac{\kappa N_\alpha}{\kappa N_A + N_B}.$$ (18)

In the extreme case when $\Delta\Psi_\alpha = 0$ or $\kappa = 1$,

$$\eta = N_\alpha/N,$$

which offers a uniform distribution of α-atoms in the interlattice sites of quasi-crystal of molten metal. The distribution of α depends in general on the value of κ or $\Delta\Psi_\alpha$ as expressed by equations (1) and (18).

c) Thermodynamical functions and equation of saturation absorption

The atom group in which the distribution of atoms is expressed by equation (1) have the following thermodynamical functions when the functional form of η expressed by (18) is adopted.

The free energy G^m is derived from equation (13) as

$$G^m = \tfrac{1}{2}(N_A\Psi_A + N_B\Psi_B) + N_\alpha\Psi_{B\alpha}$$
$$- kT\left[N_A\ln\frac{J_A}{N_A} + N_B\ln\frac{J_B}{N_B} + N_\alpha\ln\frac{J_\alpha}{N_\alpha} + N\ln N + N'\ln N' - N_0\ln N_0\right]$$
$$+ z'\,kT\,N_\alpha\ln\frac{N}{\kappa N_A + N_B}.$$ (19)

In the calculation it was approximately adopted that $1 - \eta \fallingdotseq 1$, $N_B - N_\alpha + N_A\eta \fallingdotseq N_B$ and $N_0 \fallingdotseq N$, because we confined ourselves only to poor absorber in this report.

The chemical potential μ_α^m of a α-atom in the alloy is expressed as

$$\mu_\alpha^m = \partial G^m/\partial N_\alpha = \Psi_{B\alpha} - kT\ln\frac{N'J_\alpha}{N_\alpha} + z'\,kT\ln\frac{N}{\kappa N_A + N_B}.$$ (20)

The absolute activity λ_α^m of a α-atom in the alloy is expressed as

$$\lambda_\alpha^m = \frac{N_\alpha}{N'J_\alpha}\left[\frac{N}{\kappa N_A + N_B}\right]^{z'}e^{\Psi_{B\alpha}/kT}.$$ (21)

From the equilibrium condition between gas and metal phase, $\lambda_\alpha^m = \lambda_\alpha^g\exp(\chi_d/2kT)$, the equation of absorption is derived as follows :

$$\frac{N_\alpha}{N'} = \lambda_\alpha^g J_\alpha\,e^{-\frac{\Psi_{B\alpha}+\chi_d/2}{kT}}\;\kappa^{z'}\left(\frac{N_A+N_B/\kappa}{N}\right)^{z'}$$
$$= \lambda_\alpha^g J_\alpha\,e^{-\frac{\Psi_{A\alpha}+\chi_d/2}{kT}}\left(\frac{N_A}{N} + \frac{N_B}{N\kappa}\right)^{z'}.$$ (22)

In equation (22), $\lambda_\alpha^g J_\alpha \exp\left(-\frac{\Psi_{A\alpha}+\chi_d/2}{kT}\right)$ is the absorption value of gas α by pure metal A (compare with equation (12) in the former Report I) ; N_α/N' is the absorption value (mole fraction) of α by the alloy, and N_B/N is the concentration (mole fraction) of metal B of the alloy.

Denoting $\lambda_\alpha^g J_\alpha \exp\left(-\frac{\Psi_{A\alpha}+\chi_d/2}{Tk}\right)$, N_α/N' and N_B/N by y_0, y and x, respectively, equation (22) is reduced to

$$y = y_0\left(1 - x + \frac{x}{\kappa}\right)^6.$$ (22')

It is clear from the process of calculation in which Ψ_1, $\Psi_{\alpha\alpha}$ and N_α were neglected approximately that equation (22) or (22') may hold for the absorption of diatomic gas by binary alloys which are poor absorbers.

III. Comparison of the theoretical formula with experimental results

The theoretical formula (22) or (22') will be checked hereafter mainly by the author's data on the absorption of nitrogen by molten iron alloys, namely, Fe-Ni, Fe-Cr, Fe-Mn, Fe-Si and Fe-C binary alloys.

Among these, the data on Fe-Si and Fe-C systems will be left out of the present considerations, because the constitution of Fe-Si melt is somewhat different from that of the ordinary binary melt as mentioned in the former report and the accuracy of data on Fe-C system is not as good as that of other systems for the reason formerly reported.

Now, the value of κ varies from one kind of alloy system to another.   In order to verify the present theory, the calculated curves of equation (22) which correspond to a number of κ-values are compared in Figs. 1 and 2 with the experimental results. The curves in Fig. 1 are those when $\kappa > 1$ or $|\Psi_{A\alpha}| > |\Psi_{B\alpha}|$.   Such a case occurs, for example, when nitrogen gas is absorbed by Fe-Ni alloys.   The curves in Fig. 2 are those when $\kappa < 1$ or $|\Psi_{A\alpha}| < |\Psi_{B\alpha}|$.   The absorption of nitrogen by molten Fe-Cr and Fe-Mn alloys corresponds to this case.

From the above two figures it is found that the experimental values of Fe-Ni and Fe-Mn alloys are expressed satisfactorily by the curves which correspond to $\kappa \doteqdot 2$ and $\kappa \doteqdot 0.6$, respectively.   However, in the case of Fe-Cr alloys the difference between the theory and experimental results becomes large with the increase of chromium content or with the increase of gas absorption, though experimental results in low per cent of chromium coincide with the theory.   In other words, the higher the chromium content becomes, the larger the difference between the theory and experiment becomes.

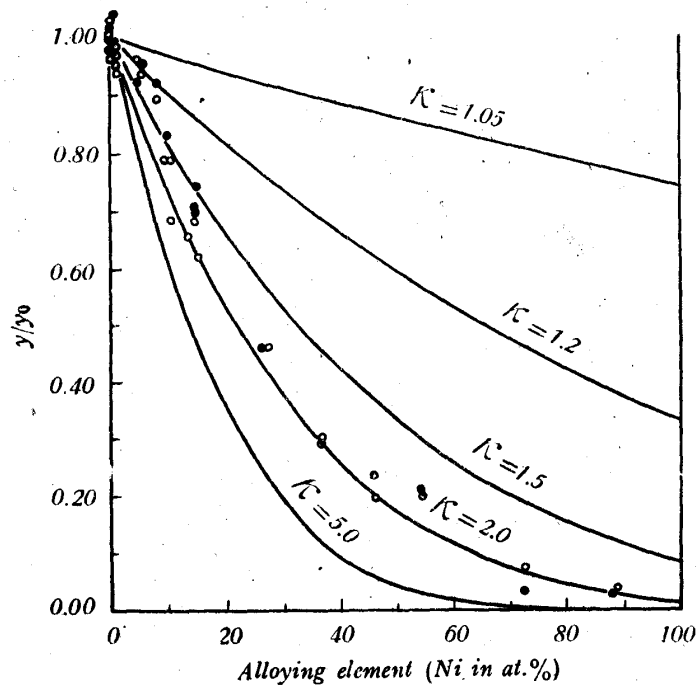This is natural because equation (22) was derived from the assumption of poor

Fig. 1 Comparison between the theoretical formula (22′) and experimental values on the absorption of nitrogen by molten Fe-Ni alloys.
- ● By means of method I (Saitô)
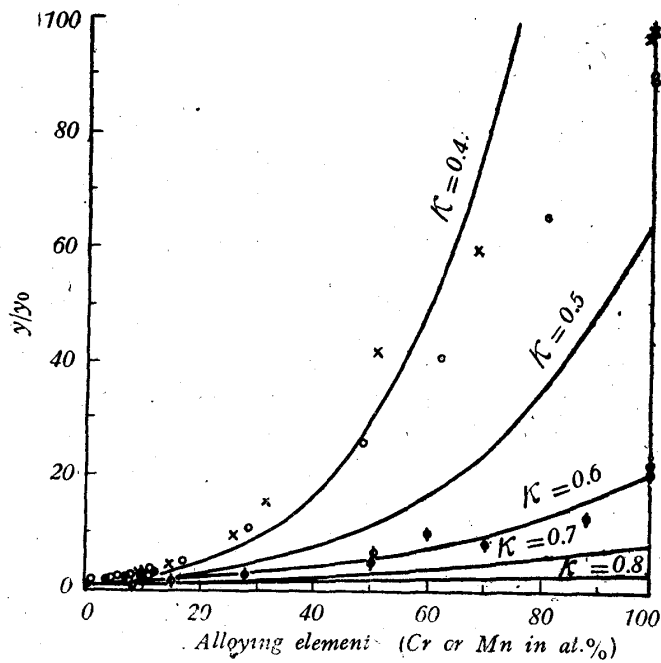- O By means of method II (Saitô)

Fig. 2 Comparison between the theoretical formula (22′) and experimental values on the absorption of nitrogen by molten Fe-Cr and Fe-Mn alloys.
- ● Fe-Cr alloys, by means of method I (Saitô)
- O Fe-Cr alloys, by means of method II (Saitô)
- × Fe-Cr alloys (Brick, Creevy)
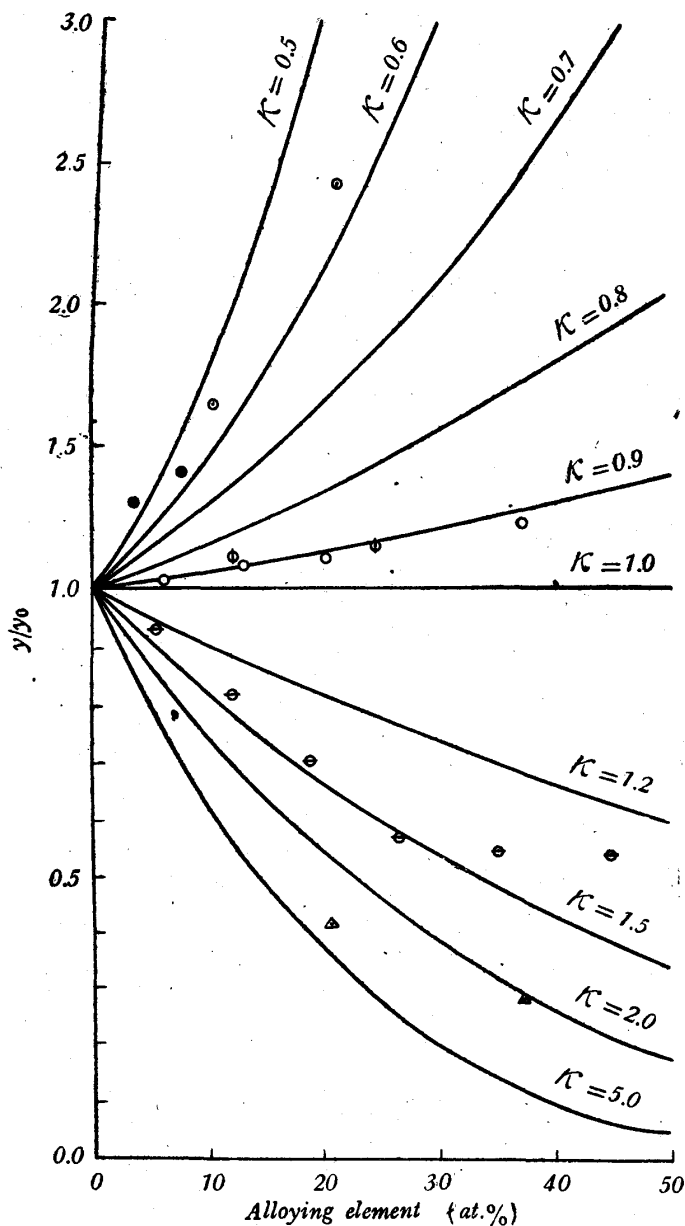- ɸ Fe-Mn alloys (Saitô)

Fig. 3 Comparison between the theoretical formula (22′) and experimental
values on the absorption of hydrogen by molten copper alloys (Sieverts).

⊙ Cu-Ni,   ● Cu-Pt,   ⌽ Cu-Au,   O Cu-Ag,   ⊖ Cu-Sn,   △ Cu-Al

absorber. In the case of good absorber the interaction energy $\Psi_{\alpha\alpha}$ between dis-
solved gas atoms should not be neglected.

Further, as is clear from the assumptions taken in the present report,
equation (22) or (22′) should hold not only for the absorption by molten alloys
but also for that by solid solutions. Some examples will be given below con-
cerning previous data on the absorption of nitrogen, hydrogen and oxygen by
binary liquids and solid solutions.

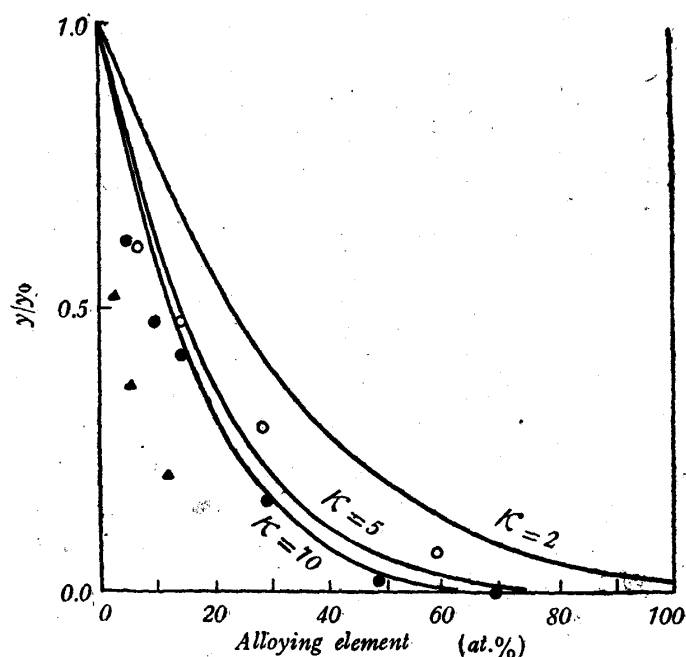Fig. 3 shows the absorption data of hydrogen by several molten copper

Fig. 4 Comparison between the theoretical formula (22′) and experimental values.

△ exp. values on the absorption of oxygen by Ag-Au alloys at 800°C (Toole, Johnson)

○ those of nitrogen by Fe-Co alloys at 1000°C (Iwasé, Fukushima)

● those of nitrogen by Fe-Ni alloys at 1000°C (Iwasé, Fukushima)

alloys by Sieverts.[4] Comparing the data with the theoretical curves, it is found that the data do not always agree with the theory. But, the disagreement can not always be attributed to the imperfection of the present theory, because these data are old ones and too much reliability cannot be expected on the accuracy.

There are shown in Fig. 4 some typical data by Toole and Johnson[5] on the absorption of oxygen by Ag-Au alloys at 800°C under several oxygen partial pressures and those by Iwasé and Fukushima[6] on the absorption of nitrogen by Fe-Ni and Fe-Co alloys at 1000°C. These are compared with the theoretical curves.

It may be concluded from the above figures that equation (22) or (22′) may be considered at present as a general absorption formula for poor absorbers, though in many results previously reported some are inaccurate and some cannot be interpreted satisfactorily by equation (22) or (22′).

Summary

Dissolved gas atoms α such as nitrogen, hydrogen or oxygen situate in the interlattice positions of binary alloy AB. The distribution of α depends upon

(4)   A. Sieverts, Z. Metallk., **21** (1929), 37.

(5)   F. J. Toole, and F. M. G. Johnson, J. Phys. Chem., **37** (1933), 331.

(6)   K. Iwasé and M. Fukuishma, Japan Inst. Metals, **1** (1937), 289.

the interaction energies $\Psi_{A\alpha}$, $\Psi_{B\alpha}$ and, etc.

The theoretical formula (22) or (22′) for the absorption of diatomic gas by binary molten alloys or solid solutions which are poor absorbers were derived according to the following process :

(1) At first, the distribution of atoms A, B and α was generally represented by introducing $\kappa \equiv \exp\left(-\dfrac{\Psi_{A\alpha}-\Psi_{B\alpha}}{z'kT}\right)$ as a parameter.

(2) The thermodynamical functions of the system consisting of A, B and α atoms were derived.

(3) From the equilibrium relation between the system and gas phase, the general absorption equation for poor absorbers was obtained.

The theoretical formula (22) or (22′) thus obtained could interprete satisfactorily the absorption of nitrogen by molten iron alloys. Further, the theory was also checked by the previous data on the absorption of hydrogen, nitrogen and oxygen by binary alloys.