

On Chemical Resistance.

By

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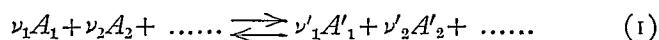
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It seems quite reasonable to choose the velocity of a reacting system as the measure of the affinity of that system; but this is a merely superficial observation, because the velocity of a reacting system is not only a function of chemical affinity, but of temperature, pressure, light, catalyser etc. For instance, notwithstanding the great affinity of the detonating gas mixture of hydrogen and oxygen, its reacting velocity at room temperature is so slight that its practical measurement is impossible. Thus we have a very interesting problem concerning the relation between the chemical affinity of a system and its velocity of reaction. Nernst¹ introduced the term *chemical resistance* with a definite meaning to express the relation.

The author here represents a study on the amount of chemical resistance and its signification.

Definition of Chemical Resistance.

As an expression of a reaction we will use the following :



where $A_1, A_2, \dots A'_1, A'_2, \dots$ are reacting substances and $\nu_1, \nu_2, \dots \nu'_1, \nu'_2, \dots$ their molecular coefficients. The reaction must proceed in such a manner that the free energy of the system shall diminish as required by the second law of thermodynamics, and the rate of diminution of the free energy be controlled by the resistance of the reacting system against the work done by this reaction. Nernst has expressed this reaction in a form analogous to the Ohm's law in electricity, namely

¹ Theoretische Chemie, 7. Aufl, p 705 (1913).

$$\text{Chemical resistance} = \frac{\text{Chemical force}}{\text{Velocity}}$$

or

$$\frac{dx}{dt} = \frac{F}{\mathfrak{R}} \quad (2)$$

where $\frac{dx}{dt}$ is the velocity of the reaction and x the number of gram-equivalents per litre transformed during the reaction. F and \mathfrak{R} designate the chemical force and resistance respectively. Let E be the free energy of this system, then $-\frac{dE}{dx}$ is the rate of diminution of the free energy during the reaction, namely chemical force or, in other words, a true expression of chemical affinity at that instant. Thus we have the following relation:

$$\text{Chemical resistance} = \frac{\text{Affinity}}{\text{Velocity}}.$$

Calculation of Affinity.

We can not determine the absolute amount of free energy of any system, but only estimate its diminution, namely the maximum work done, from the concentrations of reacting substances at the initial state of the system and those of the final state. If A designate the maximum work done by this system to establish the equilibrium, then

$$-\frac{dE}{dx} = \frac{dA}{dx} \quad (3)$$

It has been shown by van't Hoff that the maximum work done during the reaction (1) will be expressed by

$$\mathfrak{A} = RT \ln \frac{C_1^{\nu_1} C_2^{\nu_2} \dots}{C_1^{\nu_1'} C_2^{\nu_2'} \dots} + RT \ln K \quad (4)$$

where \mathfrak{A} is maximum work and C_1, C_2, \dots are the concentrations of the reacting substances before the reaction. K stands for $K = \frac{c_1^{\nu_1'} c_2^{\nu_2'} \dots}{c_1^{\nu_1} c_2^{\nu_2} \dots}$, c_1, c_2, \dots being the concentrations when the equilibrium was attained, and is the equilibrium constant. But it must be noted that the above formula of maximum work does not express the real maximum work done by the actual reaction; it is only an expression of maximum work done when the reacting substances on the left side of the equa-

tion are completely transformed into those on the right side according to the scheme of the equation, all substances maintaining their initial concentrations during the reaction.

Now we will calculate the maximum work for a more actual case, that is, the work done during the progress of the reaction towards the equilibrium in a gaseous system, or in a dilute solution, where simple gas laws are applicable. If we denote the initial state and the final or equilibrium state of the reaction by (I) and (II), and their free energies by F_1 and F_2 respectively, we have.

$$A = F_1 - F_2.$$

$$\text{Now} \quad F = U - TS, \quad \Phi = S - \frac{U + pV}{T}$$

where U is the total energy of this system, S entropy and Φ thermodynamical potential.

$$\text{Then} \quad T\Phi = TS - U - pV = -F - pV,$$

$$\text{therefore} \quad F = -pV - T\Phi = -(R + \Phi)T$$

$$\text{and we have} \quad A = F_1 - F_2 = -(R + \Phi_1)T + (R + \Phi_2)T = T(\Phi_2 - \Phi_1). \quad (5)$$

That is to say the maximum work is equal to the product of the difference of the thermodynamical potential and the absolute temperature.

Let $\phi_1^I, \phi_2^I, \dots$ be the molecular potential of the reacting substances in the initial state, and $\phi_1^{II}, \phi_2^{II}, \dots$ be those in the equilibrium state, then

$$\left. \begin{aligned} \Phi_1 &= \sum n_1^I \phi_1^I = \sum n_1^I (\bar{\phi}_1 - R \ln C_1) \\ \Phi_2 &= \sum n_1^{II} \phi_1^{II} = \sum n_1^{II} (\bar{\phi}_1 - R \ln c_1) \end{aligned} \right\} \quad (6)$$

where n_1^I, n_2^I, \dots and C_1, C_2, \dots are the numbers of mols and the concentration of A_1, A_2, \dots in the initial state, and $n_1^{II}, n_2^{II}, \dots$ and c_1, c_2, \dots those in the final state respectively, and Σ in eq. (6) refers obviously to all substances partaking in the reaction on both sides of the equation. And $\bar{\phi}_1, \dots$ are functions relating only to temperature and pressure, and independent of concentrations. If the reaction proceeded isothermally under a constant pressure, these functions would remain constant during the reaction. Now we may calculate A from eq. (6).

$$\begin{aligned} \Phi_2 - \Phi_1 &= \sum n_1^{II} (\bar{\phi}_1 - R \ln c_1) - \sum n_1^I (\bar{\phi}_1 - R \ln C_1) \\ &= \sum (n_1^{II} - n_1^I) \bar{\phi}_1 - \sum n_1^{II} R \ln c_1 + \sum n_1^I R \ln C_1 \end{aligned}$$

Adding the terms $+\sum n_1^I R \ln c_1 - \sum n_1^{II} R \ln C_1$ to the above expression, it follows that

$$\Phi_{II} - \Phi_I = \Sigma(n_1^{II} - n_1^I)\bar{\phi}_1 - \Sigma(n_1^{II} - n_1^I)R\ln c_1 + R\Sigma n_1^I(\ln C_1 - \ln c_1). \quad (7)$$

If the system be in equilibrium

$$\Sigma(\bar{\phi}_1 - R\ln c_1)\nu_1 = 0$$

$$\text{or} \quad \nu_1 \ln c_1 + \nu_2 \ln c_2 + \dots = \frac{\nu_1 \bar{\phi}_1 + \nu_2 \bar{\phi}_2 + \dots}{R} = \ln K \quad (8)$$

where K is the equilibrium constant and to the molecular coefficients of substances on the right side of the reaction scheme (I) ν_1', ν_2', \dots negative sign are assigned.

From (8) it follows

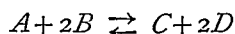
$$\begin{aligned} \Phi_{II} - \Phi_I &= \frac{n_1^{II} - n_1^I}{\nu_1} \Sigma \nu_1 \bar{\phi}_1 - \frac{n_1^{II} - n_1^I}{\nu_1} \Sigma R \nu_1 \ln c_1 + R \Sigma \frac{n_1^I}{\nu_1} (\ln C_1^{\nu_1} - \ln c_1^{\nu_1}) \\ &= \frac{n_1^{II} - n_1^I}{\nu_1} R \ln K - \frac{n_1^{II} - n_1^I}{\nu_1} R \ln K + R \Sigma \frac{n_1^I}{\nu_1} (\ln C_1^{\nu_1} - \ln c_1^{\nu_1}) \\ &= R \Sigma \frac{n_1^I}{\nu_1} (\ln C_1^{\nu_1} - \ln c_1^{\nu_1}). \end{aligned}$$

The reason, that in the above expression, $\frac{n_1^{II} - n_1^I}{\nu_1}$ can be placed outside of Σ , is as follows: Let the change of number of mols of A_1, A_2, \dots during the reaction be dn_1, dn_2, \dots , then the relation $dn_1 : dn_2 : \dots = \nu_1 : \nu_2 : \dots$ always holds, and $n_1^{II} - n_1^I = - \int dn_1$, therefore $\frac{n_1^{II} - n_1^I}{\nu_1}, \dots$ are all equal to one another.

Now we have

$$\begin{aligned} A &= T(\Phi_{II} - \Phi_I) = RT \Sigma \frac{n_1^I}{\nu_1} (\ln C_1^{\nu_1} - \ln c_1^{\nu_1}) \\ &= RT \Sigma n_1^I (\ln C_1 - \ln c_1). \end{aligned} \quad (9)$$

This is certainly the value of A in the expression $-\frac{dE}{dx} = \frac{dA}{dx}$, which express the affinity at any instant during the reaction. Now by means of equation (9) we will elucidate the method of calculation of the maximum work \mathfrak{A} , found in van't Hoff's expression. For simplicity, the following reaction will be taken



when one mol of A and two mols of B act, the maximum work A_a is given by (9) as follows:

$$\begin{aligned} A_a &= RT \sum \frac{n_1^I}{\nu_1} (\ln C_1^{\nu_1} - \ln c_1^{\nu_1}) \\ &= RT \frac{1}{1} \ln C_A + RT \frac{2}{2} \ln C_B^2 - RT \frac{1}{1} \ln c_A - RT \frac{2}{2} \ln c_B^2 \\ &= RT \ln C_A C_B^2 - RT \ln c_A c_B^{2*}. \end{aligned}$$

On the other hand, let the maximum work, when one mol of C and two mols of D act, be A_b , then we have similarly

$$A_b = RT \ln C_C C_D^2 - RT \ln c_C c_D^2$$

And the difference $A_a - A_b$ is the maximum work done when one mol of A and two mols of B have transformed into one mol of C and two mols of D , that is

$$\begin{aligned} \mathcal{A} &= A_a - A_b = RT \ln C_A C_B^2 - RT \ln c_A c_B^2 - RT \ln C_C C_D^2 + RT \ln c_C c_D^2 \\ &= RT \ln \frac{C_A C_B^2}{C_C C_D^2} - RT \ln \frac{c_A c_B^2}{c_C c_D^2} = RT \ln \frac{C_A C_B^2}{C_C C_D^2} + RT \ln K. \end{aligned}$$

Now we will calculate the expression for affinity $\frac{dA}{dx}$. When $\sum \nu_1$ is zero, that is, when during the reaction the total number of mols do not change, or, in the case of dilute solution, when the number of mols transformed is negligible in composition with the total number of mols, we have

$$C_1 = \frac{n_1^I}{N} \quad n_1^I = NC_1$$

where N is the total number of mols.

Then,
$$A = RTN \sum C_1 (\ln C_1 - \ln c_1). \quad (10)$$

The maximum work done when the concentration was diminished by x equivalents :

$$A_{-x} = RTN \sum (C_1 - \nu_1 x) \{ \ln (C_1 - \nu_1 x) - \ln c_1 \}.$$

Thus, chemical force or chemical affinity is

$$F = \frac{dA}{dx} = \frac{d[RTN \sum (C_1 - \nu_1 x) \{ \ln (C_1 - \nu_1 x) - \ln c_1 \}]}{dx}$$

where
$$\frac{d\{(C_1 - \nu_1 x) \ln (C_1 - \nu_1 x)\}}{dx} = -\nu_1 (\ln (C_1 - \nu_1 x) + 1),$$

* The limiting values of $n_C \ln C_C, n_D \ln C_D$ when $x=0$ are equal to zero.

$$\frac{d\{(C_1 - \nu_1 x) \ln c_1\}}{dx} = -\nu_1 \ln c_1.$$

Therefore we have $\frac{dA}{dx} = RTN \{-\Sigma \ln (C_1 - \nu_1 x)^{\nu_1} - \Sigma \nu_1 + \Sigma \ln c_1^{\nu_1}\}$
 $= RTN \{\Sigma \ln (C_1 - \nu_1 x)^{-\nu_1} + \Sigma \ln c_1^{\nu_1}\}. \quad (11)$

But, when during reaction some change takes place in the number of mols in the system, $\Sigma \nu_1$ is not equal to zero. In such a case let number of mols of the initial system be N and the change in the number of mols when the concentration is diminished by x equivalents,

$$N = n_1 + n_2 + \dots + n'_1 + n'_2 + \dots$$

$$\Delta N = (n_{1,x} - n_1) + (n_{2,x} - n_2) + \dots + (n'_{1,x} - n'_1) + (n'_{2,x} - n'_2) + \dots$$

where $n_{1,x}$, $n_{2,x}$, are the numbers of mols A_1 , A_2 , after the said change in the concentration.

Putting $n_{1,x} - n_1 = \Delta n_1$, $n_{2,x} - n_2 = \Delta n_2$,

we have $\Delta N = \Sigma \Delta n_1 = \Sigma \frac{\Delta n_1}{\nu_1} \nu_1 = \frac{\Delta n_1}{\nu_1} \Sigma \nu_1.$

As formerly stated, $\frac{\Delta n}{\nu}$ is identical for all substances, and putting $\frac{\Delta n}{\nu} = a$, we get

$$\Delta N = a \Sigma \nu_1.$$

Let $C_{1,x}$, $C_{2,x}$, be the concentrations after the said change in the concentration, then

$$\begin{aligned} C_{1,x} &= \frac{n_{1,x}}{N + \Delta N} = \frac{n_1 + \Delta n_1}{N + \Delta N} = \frac{n_1}{N + \Delta N} + \frac{\Delta n_1}{N + \Delta N} \\ &= \frac{\frac{n_1}{N}}{1 + \frac{\Delta N}{N}} + \frac{\nu_1 \Delta n_1}{\nu_1 (N + \Delta N)} = \frac{C_1}{1 + \frac{\Delta N}{N}} - \nu_1 x. \end{aligned}$$

Again $C_1 = \frac{n_1}{N}$, $x = \frac{-\Delta n_1}{\nu_1 (N + \Delta N)}$

Therefore $x = \frac{-\Delta n_1}{\nu_1 (N + \Delta N)} = -a \frac{1}{(N + \Delta N)} = -\frac{\Delta N}{\Sigma \nu_1} \frac{1}{N + \Delta N}$

or
$$\Delta N = \frac{-N x \Sigma \nu_1}{1 + x \Sigma \nu_1}.$$

The maximum work, when the concentration is diminished by x equivalents,

$$\begin{aligned} A_{-x} &= RT(N + \Delta N) \Sigma C_{1,x} \{ \ln C_{1,x} - \ln c_1 \} \\ &= RNT \left(\frac{1}{1 + x \Sigma \nu_1} \right) \Sigma \{ C_1(1 + x \Sigma \nu_1) - \nu_1 x \} [\ln \{ C_1(1 + x \Sigma \nu_1) - \nu_1 x \} \\ &\quad - \ln c_1]. \end{aligned} \tag{12}$$

The above expression is easily differentiable by x , viz.

$$\begin{aligned} \frac{dA}{dx} &= RTN \left(\frac{1}{1 + x \Sigma \nu_1} \right) \Sigma (C_1 \Sigma \nu_1 - \nu_1) [\ln \{ C_1(1 + x \Sigma \nu_1) - \nu_1 x \} - \ln c_1 + 1] \\ &\quad + RTN \frac{\Sigma \nu_1}{(1 + x \Sigma \nu_1)^2} \Sigma \{ C_1(1 + x \Sigma \nu_1) - \nu_1 x \} [\ln \{ C_1(1 + x \Sigma \nu_1) - \nu_1 x \} \\ &\quad - \ln c_1]. \end{aligned} \tag{13}$$

Calculation of Chemical Resistance.

From the definition of (2) the chemical resistance is expressed as

$$\mathfrak{R} = \frac{-\frac{dE}{dx}}{\frac{dx}{dt}} = \frac{\frac{dA}{dx}}{\frac{dx}{dt}}.$$

For the expression of affinity $\frac{dA}{dx}$, the value of (13) in a general case or the value of (11) in the case of $\Sigma \nu_1 = 0$ or at reactions in dilute solutions, may be used. The expression of chemical velocity $\frac{dx}{dt}$ is represented in general as follows:

$$\begin{aligned} \frac{dx}{dt} &= k_1 \{ C_1(1 + x \Sigma \nu_1) - \nu_1 x \}^{\nu_1} \{ C_2(1 + x \Sigma \nu_2) - \nu_2 x \}^{\nu_2} \dots \\ &\quad - k_2 \{ C_1'(1 + x \Sigma \nu_1') - \nu_1' x \}^{-\nu_1'} \{ C_2'(1 + x \Sigma \nu_2') - \nu_2' x \}^{-\nu_2'} \dots \end{aligned}$$

when $\Sigma \nu' = 0$ or the reaction occurs in a dilute solution, this expression becomes more simple.

$$\frac{dx}{dt} = k_1 (C_1 - \nu_1 x)^{\nu_1} (C_2 - \nu_2 x)^{\nu_2} \dots - k_2 (C_1' - \nu_1' x)^{-\nu_1'} (C_2' - \nu_2' x)^{-\nu_2'} \dots$$

where k_1 is the velocity constant for the change from left to right in the reaction scheme and k_2 that of the opposite reaction. Moreover we have the relation $\frac{k_1}{k_2} = K$, when K is the equilibrium constant.

As one example of calculation of the chemical resistance, we will take the following reaction scheme :



Let the initial concentrations of A, B, C, D be a, b, c, d , and those of the final equilibrium state $(a - \xi), (b - 2\xi), c + \xi, (d + 2\xi)$, then from (I I) the affinity of this reaction is

$$\begin{aligned} F &= \frac{dA}{dx} = RTN \ln \frac{(c+x)(d+2x)^2}{(a-x)(b-2x)^2} + RTN \ln \frac{(a-\xi)(b-2\xi)^2}{(c+\xi)(d+2\xi)^2} \\ &= RTN \ln \frac{(c+x)(d+2x)^2}{(a-x)(b-2x)^2} - RTN \ln K. \end{aligned}$$

Therefore

$$\mathfrak{R} = \frac{\frac{dA}{dx}}{\frac{dx}{dt}} = \frac{RTN \ln \frac{(c+x)(d+2x)^2}{(a-x)(b-2x)^2} - RTN \ln K}{k_1 (a-x)(b-2x)^2 - k_2 (c+x)(d+2x)^2} \cdot (14)$$

This expression represents the chemical resistance as a function of x , and we can calculate it for all values of x from $x=0$ to $x=\xi$. At the limiting case, however, were $x=\xi$ and consequently $\mathfrak{R} = \frac{0}{0}$, it is indeterminate, but after the usual method, we get for it the following

$$\lim_{x \rightarrow \xi} \mathfrak{R} = \frac{RTN \frac{4ABCD(B+D) + BD(ABD + CBD)}{AB^2CD^2}}{-k_1 B(B+4A) - k_2 D(D+4C)}$$

where A, B, C, D denote $(a-2x), (b+x), (c-x), (d+2x)$ respectively, and this limiting value is definite.

Signification of Chemical Resistance.

In the preceding sections the calculation of chemical resistance according to the principle of thermodynamics had been considered.

Now we are in a position to examine the signification of chemical resistance and for this purpose must make use of the idea of atom and molecule.

If there are two substances, *A* and *B*, they attract each other by the universal force of attraction; but in certain cases, according to their nature, another kind of attraction, namely chemical affinity, may act between them. Z. Gruwitsch¹ distinguished these two kinds of attractive force in the following way:

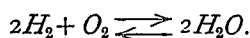
I Physical attractive force:

- a) It is not specific;
- b) its sphere of action is not limited;
- c) its action on a given mass is independent of the existence of other masses;
- d) its action is not atomistic, that is, it acts as a whole all over the closed surface and not in singular rays.

II Chemical attractive force:

- a) It is specific;
- b) its sphere of action is limited, probably to an atomic distance;
- c) its action on a given mass is different; according as one part of the force has already been saturated by another substance, or not;
- d) its action is atomistic, that is, it expresses itself by leaps in a few singular rays.

Under the supposition that chemical affinity has the above mentioned character, we will now consider the following special case as an example:



According to the above consideration, H_2 and O_2 would at first dissociate, and then when they approach each other within the atomic distance, the affinity will begin to act. The amount of the affinity is dependent not only on the concentrations of H and O , but also on that of H_2O already formed, as described under (c). Let the characteristic constant of the affinity between H_2 and O_2 be κ , then the actual amount of the affinity is a function of the concentrations H_2O , H and O which contains the characteristic constant κ viz.,

$$F = f(C_H, C_O, C_{H_2O}, \kappa).$$

¹ Zs. physik. Chem., 87, 331, (1914).

On the other hand from (11), we have

$$F = \frac{dA}{dx} = RTN \{ \sum \ln (C_1 - \nu_1 x)^{-\nu_1} + \sum \ln c_1^{\nu_1} \}.$$

Here the value of (13) must have been used, but for the sake of simplicity we have taken the above expression. As seen from it, the first term is only a simple function of C_H , C_O and C_{H_2O} and does not contain the constant x , and so the second term must contain it, but in all reactions with the same initial concentrations the second term is independent of x and consequently of C_H , C_O and C_{H_2O} . Therefore the second term itself must be a constant, namely

$$x = \sum \ln c_1^{\nu_1}$$

This is nothing but the well known mass law.

If we consider the chemical affinity and the mechanism of a chemical reaction as above described, the signification of chemical resistance is then clear. It consists from two terms of different properties. In the above example, they are :

1. The resistance to the dissociation of the molecules, H_2 and O_2 to atoms.
2. The probability that H and O approach each other within atomic distance by their kinetic energies.

With our present knowledge about atoms and molecules, it is impossible to calculate chemical resistance in a direct way.
