

SIMPLE RELATION FOR THE DETERMINATION OF FREE ACTIVATION ENTHALPIES OF CONFORMATIONAL TRANSITIONS*

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A plot of the logarithm of absorbance ratio of conformationally sensitive infrared bands against reciprocal temperature for samples measured at a constant cooling rate has the form of a curve with asymptotes intersecting at the temperature T_0 . For substances with two rotational isomers, the free activation enthalpy of the conformational transition ΔG^\ddagger may be determined from the temperature T_0 and the known cooling rate either by means of the empirical relation $dT^{-1}/dt = 1.04 \cdot 10^{10} \exp(-\Delta G^\ddagger/RT_0)$ or more precisely by means of an explicit relation derived from an analysis of kinetic equations.

In our previous papers^{1,2} we have shown that the kinetics of conformational transitions may be followed by measurements of the temperature dependence of infrared band intensities. As long as the measured substance is in thermodynamic equilibrium, the logarithm of the absorbance ratio of the conformationally sensitive bands is linearly dependent on reciprocal temperature with the slope of the dependence indicating the enthalpy difference (ΔH) between the two conformers. By analysis of a plot which deviates from a straight line, the rate of establishment of equilibrium may be determined by numerical analysis of kinetic equations. This method we have used for the determination of the activation energy of conformational transitions in chlorocyclohexane¹ and of the activation enthalpy in a series of secondary chloroalkanes².

In this paper we wish to show that it is possible to make use of the characteristic shape of the temperature dependence of the absorbance ratio of conformationally sensitive bands for a simple determination of free activation enthalpies of conformational transitions, without the use of a computer.

The determination of the temperature dependence of rate constants of chemical reactions from kinetic measurements at variable temperature has also been the subject of some other papers (see *e.g.* ref. 3 and the literature cited therein). In these the rate constants have been obtained by numerical differentiation of the obtained time dependence of the measured component concentration in the reaction mixture. In our experimental setup which permits concentration measurements in intervals of three minutes or longer, the numerical differentiation of the concentration plot

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is not possible and the rate constants can only be obtained by integration of the kinetic equations at variable temperature, as has been done in the papers^{1,2}, as well as in the present one.

Analysis of the Time Dependence of the Conformer Concentration Ratio at Uniform Cooling

The conformational equilibria in a substance which exists in the form of two conformers may be described by the equation

$$dc_1/dt = -(k_{12} + k_{21})c_1 + k_{21} = -(k_{12} + k_{21})(c_1 - c_1^b), \quad (1)$$

where $c_1^b = k_{21}/(k_{12} + k_{21})$ is the equilibrium concentration of the first component. At constant temperature the rate constants are time independent and the equation has the solution

$$c_1(t) = c_1^b + (c_1^0 - c_1^b) \exp [-(k_{12} + k_{21})t], \quad (2)$$

where c_1^0 is the concentration of the first component at time zero. If the temperature is varied with time, the constant k_{12} and k_{21} are time dependent. The solution of equation (1) is then obtained in the form

$$c_1(t) = e^{-\int (k_{12}(t) + k_{21}(t)) dt} \int k_{21}(t) \cdot e^{\int [k_{12}(t) + k_{21}(t)] dt} dt. \quad (3)$$

Further analysis will concern the case where $1/T$ is a linear function of time ($1/T = at$), and the rate constants correspond to the Arrhenius relation

$$k_{21} = A_2 \exp(-E_2^*/RT), \quad k_{12} = A_1 \exp(-E_1^*/RT).$$

For this case we obtain $\int (k_{12}(t) + k_{21}(t)) dt = -(A_1/b_1) \exp(-b_1t) - (A_2/b_2) \cdot \exp(-b_2t)$, so that

$$\begin{aligned} c_1(t) = & \{ \exp [(A_1/b_1) e^{-b_1t} + (A_2/b_2) e^{-b_2t}] \} \cdot \\ & \cdot \{ c_1^0 \exp [-(A_1/b_1) e^{-b_1t_0} - (A_2/b_2) e^{-b_2t_0}] + \\ & + \int_{t_0}^t A_2 e^{-b_2x} \exp [-(A_1/b_1) e^{-b_1x} - (A_2/b_2) e^{-b_2x}] dx \} \end{aligned} \quad (4)$$

where $b_1 = aE_1^*/R$, $b_2 = aE_2^*/R$ and a is the rate of cooling. After performing the

substitution $z = (A_2/b_2) \exp(-b_2x)$ in the integral of Eq. (4), then $dz = -A_2 \cdot \exp(-b_2x) dx$, $(A_1/b_1) \exp(-b_1x) = Bz^\alpha$, where $\alpha = b_1/b_2 = E_1^*/E_2^*$ and $B = (A_1/b_1)(A_2/b_2)^{-\alpha}$. In this way the integral of Eq. (4) assumes the form $\int \exp(-x - Bx^\alpha) dx$ with limits from $(A_2/b_2) \exp(-b_2t_0)$ to $(A_2/b_2) \exp(-b_2t)$. Introducing the function $F(x, \alpha, B) = \exp(x + Bx^\alpha) \int_x^\infty \exp(-u - Bu^\alpha) du$, Eq. (4) is obtained in the form

$$c_1(t) = F\left[\left(\frac{A_2}{b_2}\right) e^{-b_2t}, \alpha, B\right] + \left\{c_1^0 - F\left[\left(\frac{A_2}{b_2}\right) e^{-b_2t_0}, \alpha, B\right]\right\} \times \quad (5)$$

$$\times \exp\left[\left(A_1/b_1\right) e^{-b_1t} + \left(A_2/b_2\right) e^{-b_2t} - \left(A_1/b_1\right) e^{-b_1t_0} - \left(A_2/b_2\right) e^{-b_2t_0}\right].$$

If we begin the cooling from a temperature where k_{21} is large compared to b_2 (i.e. from a temperature where the reaction rate is still so large that equilibrium is maintained in the system), the second member of this expression is negligible for values of t only slightly larger than t_0 (the factor $\exp[(-A_2/b_2) e^{-b_2t_0} + (A_2/b_2) e^{-b_2t}]$ is small). We then obtain

$$c_1(t) = F\left[\left(\frac{A_2}{b_2}\right) e^{-b_2t}, \alpha, B\right]. \quad (6)$$

An analysis of the properties of the function $F(x, \alpha, B)$ as well as directions for a numerical calculation of its values are given in the Appendix.

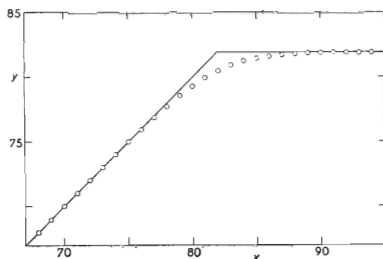


FIG. 1

Calculated Curve of the Logarithm of Concentration Ratio $y = \log_{10}(c_1/c_2) \cdot 10^2$ vs Logarithm of Equilibrium Concentration Ratio $x = \log_{10}(c_1^0/c_2^0) \cdot 10^2$ for the Case that the Ratio of Activation Enthalpies for the Transition of Two Conformers $\Delta H_1^*/\Delta H_2^* = 1.04$ and for $B = 0.15$.

Numerical evaluation of this function has been made for the values $\alpha = 1.04$; $B = 0.15$; $x = (A_2/b_2) \exp(-b_2 t) = (\alpha B \cdot 10^{\alpha})^{1/(1-\alpha)}$; $z = 0.67$ to 0.95 with a step 0.01 ; z has the meaning of $\log_{10}(c_1^b/c_2^b)$ in the time considered. From the calculated value $c_1(t)$ we calculated $\log_{10}[c_1(t)/(1 - c_1(t))]$, which we plotted against $\log_{10} \cdot (c_1^b/c_2^b)$ (Fig. 1).

From Fig. 1 it can be seen that for $z < 0.76$, $\log_{10}(c_1/c_2)$ differs from $\log_{10} \cdot (c_1^b/c_2^b)$ by less than 0.001 . For $z > 0.89$, $\log_{10}(c_1/c_2)$ differs from the limit value for $t = \infty$, $\log_{10}(c_1^\infty/c_2^\infty) = 0.8189$, by less than 0.001 . Between these values, a relatively sharp transition from the asymptote $\log_{10}(c_1/c_2) = \log_{10}(c_1^b/c_2^b)$ to the asymptote $\log_{10}(c_1/c_2) = 0.818856$ takes place. The limit value of $\log_{10}(c_1/c_2)$ for $1/T \rightarrow \infty$ can be easily obtained experimentally by following the plot of $\log_{10}(c_1/c_2)$ vs $1/T$. By means of this limit value of the logarithm of the concentration ratio the temperature T_0 may be defined as the temperature at which $\log_{10}(c_1^b/c_2^b) = \log_{10}(c_1^\infty/c_2^\infty)$.

Determination of the Free Activation Enthalpy of Conformational Transitions

As shown in the Appendix, par. 4, the approximate expression for c_1^∞ is

$$c_1^\infty = F(0, \alpha, B) = 1/(1 + \alpha B x_0^{\alpha-1}), \quad (7)$$

where x_0 is the solution of the equation $x_0 + \alpha B x_0^\alpha = e^{-C}$ (C is the Euler constant). By means of the relation $(1 - c_1^\infty)/c_1^\infty = c_2^b(T_0)/c_1^b(T_0)$ we obtain therefrom

$$\alpha B x_0^{\alpha-1} = (1 - c_1^\infty)/c_1^\infty = c_2^b(T_0)/c_1^b(T_0) = (A_1/A_2) \exp[-(\alpha - 1) E_2^*/RT_0]$$

and further

$$x_0^{\alpha-1} = \frac{b_2 b_1}{b_1 A_1} \left(\frac{A_2}{b_2}\right)^\alpha \frac{A_1}{A_2} \exp[-(\alpha - 1) E_2^*/RT_0] = \quad (8)$$

$$= \left(\frac{A_2}{b_2}\right)^{\alpha-1} \exp[-(\alpha - 1) E_2^*/RT_0], \quad (9)$$

or

$$k_{21}(T_0) = b_2 x_0 = a E_2^* x_0 / R. \quad (10)$$

Further we have

$$x_0 = \frac{x_0 + \alpha B x_0^\alpha}{1 + \alpha B x_0^{\alpha-1}} = e^{-C} c_1^\infty = e^{-C} c_1^b(T_0) \quad (11)$$

and therefore

$$k_{21}(T_0) = a(E_2^*/R) c_1^b(T_0) e^{-C}. \quad (12)$$

Eq. (12) determines the value k_{21}/E_2^* from the values of the rate of cooling a and from the limit concentration c_1^∞ equal to the equilibrium concentration $c_1^b(T_0)$ at temperature T_0 . The values $c_1^b(T_0)$ and a are both experimentally accessible, so that by plotting the values $\ln(k_{21}/E_2^*)$ vs $1/T_0$ for various values of cooling rate we can determine E_2^* and from it the frequency factor of the Arrhenius relation. By measuring the temperature dependence of the concentration only at one rate of cooling a , the analysis can be based on the Eyring relation

$$k_{21} = (k/h) T \exp(\Delta S_2^*/R - \Delta H_2^*/RT). \quad (13)$$

A direct solution of the kinetic equations by the application of the Eyring relation is much more complicated than the solution for the Arrhenius relation. The solution procedure is indicated in the Appendix, par. 8. However, in order to obtain the approximate relation for the rate constant at temperature T_0 , it is sufficient to replace T in the member kT/h in the Eyring equation by the expression $T_0 \exp((T - T_0)/T)$, which differs very little from T in the vicinity of T_0 (the only region seriously affecting the values of c_1); the Eyring relation can then be transformed to the Arrhenius relation with the parameters

$$A_1 = (kT_0/h) \exp(\Delta S_1^*/R + 1); \quad A_2 = (kT_0/h) \exp(\Delta S_2^*/R + 1);$$

$E_1^* = \Delta H_1^* + RT_0$; $E_2^* = \Delta H_2^* + RT_0$. By means of Eq. (12) we then obtain

$$(\Delta G_2^*/RT_0) = 24.337 - \ln[(\Delta H_2^*/RT_0) + 1] - \ln a - \ln[1 - c_1^b(T_0)] \quad (14)$$

By means of Eq. (14), the free activation enthalpy ΔG_2^* at temperature T_0 may be obtained from the known cooling rate, the limit value of the ratio of component concentrations $\log_{10}(c_1/c_2)$ and from the temperature T_0 . Besides the experimentally easily accessible quantities, relation (14) also contains the member $\ln[(\Delta H_2^*/RT_0) + 1]$. In computing ΔG_2^* we make use of the circumstance that this member is logarithmic, so that even very roughly estimated values of ΔH_2^* yield very good values of ΔG_2^* . *E.g.* by changing $(\Delta H_2^*/RT_0) + 1$ in the ratio 2 : 3, ΔG_2^* changes by 0.12 kcal/mol at 150 K. The practical procedure is to estimate ΔH_2^* and to calculate ΔG_2^* . From the thus determined ΔG_2^* we determine ΔH_2^* under the assumption that $\Delta S_2^* = 0$ or $\Delta S_2^* = (S_1 - S_2)/2$. By repeating this process, the value of ΔG_2^* can be obtained very quickly. If *e.g.* in Fig. 1 we put $a = 10^{-7}$ and $E_1^*/E_2^* = 1.04$, then suitable parameters of the Arrhenius equations are ($E_1^* = 11897$ cal/mol, $E_2^* = 11438$ cal/mol, $A_1 = 5.3955 \cdot 10^{11}$ s $^{-1}$, $A_2 = 8.5512 \cdot 10^{11}$ s $^{-1}$) and the temperature $T_0 = 161.6$ K. For this temperature the free activation enthalpy defined by the Eyring relation is for these values equal to $\Delta G_1^* = 12482$ cal/mol, $\Delta G_2^* = 11878$ cal/mol. The free activation enthalpies computed by means of relation (14),

yield the values $\Delta G_1^\ddagger = 12461$ cal/mol, $\Delta G_2^\ddagger = 11857$ cal/mol. This agreement shows that relation (14) permits determination of ΔG^\ddagger with an accuracy better than experimental possibilities.

The temperature T_0 may also be used for an approximate estimate of ΔG^\ddagger , based on the Eyring relation and the assumption that at the temperature T_0 the relative cooling rate $T(dT^{-1}/dt)$ is equal to one half of the rate constant. In this case

$$2(dT^{-1}/dt) = (k/h) \exp(-\Delta G^\ddagger/RT_0) = 2.08 \cdot 10^{10} \exp(-\Delta G^\ddagger/RT_0). \quad (15)$$

Values estimated in this way may be refined by the use of relation (14). Using the empirical relation (15), the value $\Delta G^\ddagger = 12580$ cal/mol is obtained for the above case.

For a cooling rate around $5 \cdot 10^{-7} \text{ K}^{-1} \text{ s}^{-1}$ the values of $\Delta H_2^\ddagger/RT_0 + 1$ lie in the vicinity of 35. For this value and the value $1 - c_2^b(T_0) = 0.102$ (i.e. 10.2%) Eq. (15) is identical with Eq. (14).

Example of a Determination of Free Activation Enthalpies by Means of the Derived Expressions

The molecule of chlorocyclohexane can assume two conformations, the axial and the equatorial forms⁴⁻⁷, respectively. In order to obtain the free activation enthalpy of the transition between these two forms, we have cooled the 30% solution of the sample in nujol at the rate $5 \cdot 10^{-7} \text{ K}^{-1} \text{ s}^{-1}$ with simultaneous recording of the infrared bands at 560 and 512 cm^{-1} , characteristic of the axial and equatorial forms of cyclohexane, respectively. From the plot of the logarithm of the absorbance ratio of these two bands against T^{-1} (see ref. 1, Fig. 1) we obtained from the limiting value of the absorbance ratio the value of $T_0 = 161$ K. For the ratio of absorbance coefficients¹ $\xi_{560}/\xi_{512} = 5$, $c_{ax} = 0.14$ and $c_{eq} = 0.86$ were found at T_0 . For these values by means of Eq. (15) we calculated the free activation enthalpy $\Delta G^\ddagger = 12.2$ kcal/mol and from Eq. (14) the free activation enthalpies $\Delta G_{E \rightarrow A}^\ddagger = 11.9$ kcal/mol and $\Delta G_{A \rightarrow E}^\ddagger = 11.3$ kcal/mol. In the preceding paper¹, for this system the parameters of the Arrhenius relation have been obtained by numerical integration, yielding the Eyring free activation enthalpies $\Delta G_{E \rightarrow A}^\ddagger = 11.9$ kcal/mol and $\Delta G_{A \rightarrow E}^\ddagger = 11.4$ kcal/mol. These values agree well with the values obtained from Eqs (14) and (15).

The relations (14) and (15) were used also for the calculation of free activation enthalpies for systems analyzed numerically from kinetic equations in the preceding paper². The mean quadratic deviations of the values ΔG^\ddagger obtained by means of (14) and (15) with respect to the values from the preceding paper are 0.35 kcal/mol and 0.5 kcal/mol. These results indicate that the relation (14) which was derived for a two-component reversible reaction, may in good approximation be applied also for a three-component system.

APPENDIX

In paragraphs 1–7 of this appendix, the function $F(x, \alpha, B)$ will be analyzed. In paragraph 1, the transformation of this function to an identical function of different arguments is derived; this transformation permits a transition from a range of bad convergence to a range where convergence is better. Paragraphs 2–4 are devoted to the function $F(0, \alpha, B)$. In paragraph 2, a simple series for the calculation of the function $F(0, \alpha, B)$ is derived; in addition it is shown that for $\alpha < 1$, $F(0, \alpha, B)$ is a whole transcendental function of the parameter B (according to paragraph 1, for $\alpha > 1$ it is then a whole transcendental function of $B^{-1/\alpha}$). In paragraph 3 a more complicated series is derived; for small B and α in the vicinity of 1 it converges more rapidly than the series of paragraph 2. In paragraph 4 a simple approximate relation for the value of the function $F(0, \alpha, B)$ is derived, valid for $\alpha \simeq 1$; in the text this has been used for the derivation of the relations for ΔG^\ddagger . In paragraph 5 calculation of the function $F(x, \alpha, B)$ is discussed for the range of small x , i.e. for the range where the reaction rate is already small. In paragraph 6 the function $F(x, \alpha, B)$ is derived for large x , where the reaction is rapid. In paragraph 7 the computing procedure is given for intermediate values of x for the cases where the required accuracy cannot be attained by the combination of the methods of paragraphs 5 and 6 for the whole range of x . Finally in paragraph 8 our problem is briefly formulated for the case of the Eyring rate equation.

1. In the integration defining $F(x, \alpha, B)$ we make substitution $z = Bt^\alpha$ and then integrate *per partes* with $f'(z) = B^{-1/\alpha} \cdot z^{(1/\alpha-1)} \exp(-B^{-1/\alpha} z^{1/\alpha})$; $g(z) = e^{-z}$:

$$F(x, \alpha, B) = \exp(x + Bx^\alpha) \int_x^\infty \exp(-t - Bt^\alpha) dt = 1 - F(Bx^\alpha, 1/\alpha, B^{-1/\alpha}),$$

or

$$F(x, \alpha, B) = 1 - F(Bx^\alpha, 1/\alpha, B^{-1/\alpha}). \quad (16)$$

2. For $x = 0$ the member $\exp(-Bt^\alpha)$ is developed in a Taylor series and the resulting integrals are expressed by means of the function Γ :

$$\int_0^\infty e^{-t - Bt^\alpha} dt = \sum_{k=0}^{\infty} \int_0^\infty \frac{(-B)^k t^{k\alpha}}{k!} e^{-t} dt = \sum_{k=0}^{\infty} \frac{(-B)^k \Gamma(k\alpha + 1)}{k!} \quad (17)$$

For $\alpha < 1$ this series is convergent for every B , for $\alpha > 1$ it is divergent for every B , but for small B it is semiconvergent. For $\alpha > 1$ the formula from the preceding paragraph may be used; we see that for $\alpha < 1$, $F(0, \alpha, B)$ is a whole transcendental function of B , for $\alpha > 1$ it is a whole transcendental function of $B^{-1/\alpha}$. For α near to 1 and for large B the series converges very slowly; in this range it is better to use the semiconvergent series formed by the transformation of paragraph 1. For $\alpha = 1$, $F(x, 1, B) = 1/(B + 1)$.

$$\begin{aligned} 3. \quad & \int_0^\infty \exp(-t - Bt^\alpha) dt = \int_0^\infty \exp[-(B+1)t + B(t-t^\alpha)] dt = \\ & = \frac{1}{B+1} \int_0^\infty \exp\left\{-t + \frac{B}{B+1} [t - (B+1)^{1-\alpha} t^\alpha]\right\} dt = \\ & = \frac{1}{B+1} \sum_{k=0}^{\infty} \left(\frac{B}{B+1}\right)^k \sum_{s=0}^k \frac{(-1)^s (B+1)^{s(1-\alpha)} \Gamma(k+1+s(\alpha-1))}{s!(k-s)!} = F(0, \alpha, B). \quad (18) \end{aligned}$$

If in this series the factor $(-1)^s$ is omitted, we obtain a series of positive members majorant to the original one; the sum of this majorant is equal to $\int_0^\infty \exp(-t + Bt^\alpha) dt$. As this integral exists for $\alpha < 1$ (from a certain t_0 , $Bt^\alpha < t/2$, so that the integrand is smaller than $e^{-t/2}$), also our series is convergent for $\alpha < 1$. For $\alpha < 1$ the series is divergent, but for small B and $\alpha \approx 1$ it is semiconvergent. For α in the vicinity of 1 this series converges more rapidly than the series of paragraph 2, because the sum in s is the k th difference of the function $\Gamma(k+1+x)(B+1)^{-x}/k!$ at $x=0$ with step $\alpha-1$, so that for α near to 1 this expression decreases very rapidly with increasing k . If B is small and $\alpha > 1$ near to 1, it is better to use the semiconvergent development with these parameters, instead of the transformation of paragraph 1 (the transformed series converges more slowly). This development was used for a numerical computation of the function $F(0, 1.04, 0.15) = 0.868240$ using the calculator Sharp PC-1002.

$$4. \int_0^\infty \exp(-t - Bt^\alpha) dt = \int_0^\infty \exp[-(1 + \alpha Bx_0^{\alpha-1})t] \exp[B(\alpha x_0^{\alpha-1}t - t^\alpha)] dt. \quad (19)$$

The second member is developed in Taylor series by α in point $\alpha = 1$ and only the first two members are considered:

$$\exp[B(\alpha x_0^{\alpha-1} - t^\alpha)] \approx 1 + (\alpha - 1)B(t + t \ln x_0 - t \ln t).$$

By integration of the first member we obtain $1/(1 + \alpha Bx_0^{\alpha-1})$ the second member is integrated *per partes*

$$\begin{aligned} & (\alpha - 1)B \int_0^\infty (t + t \ln x_0 - t \ln t) \exp[-(1 + \alpha Bx_0^{\alpha-1})t] dt = \\ & = \frac{(\alpha - 1)B}{1 + \alpha Bx_0^{\alpha-1}} \{ [-\exp[-(1 + \alpha Bx_0^{\alpha-1})t] (t + t \ln x_0 - t \ln t)]_0^\infty + \\ & \quad + \int_0^\infty (1 + \ln x_0 - 1 - \ln t) \exp[-(1 + \alpha Bx_0^{\alpha-1})t] dt \} = \\ & = \frac{(\alpha - 1)B}{(1 + \alpha Bx_0^{\alpha-1})^2} [\ln x_0 + C + \ln(1 + \alpha Bx_0^{\alpha-1})], \end{aligned} \quad (20)$$

where $C = 0.5772156649$ is the Euler constant. The value of x_0 is selected so as to make the integral of the second member zero: $x_0 = \alpha Bx_0^\alpha = e^{-C}$. This equation may be solved *e.g.* so that it is transformed to the form $x_0 = e^{-C}/(1 + \alpha Bx_0^{\alpha-1})$ and solved by an iterative procedure with the first iteration $x_0^{(1)} = e^{-C}/(1 + \alpha B)$; convergence for α near to 1 and for small B is very rapid. In this way we have derived the approximate relation

$$F(0, \alpha, B) \approx 1/(1 + \alpha Bx_0^{\alpha-1}) \quad (21)$$

where x_0 is the solution of equation $x_0 + \alpha Bx_0^\alpha = e^{-C}$; this relation is valid for α near to 1 and for small B . By means of this relation we obtain *e.g.* $F(0, 1.04, 0.15) \approx 0.868371$ with an error $1.3 \cdot 10^{-4}$ as compared to the exact values.

5. Let us calculate the integral $I(x, \alpha, B) = \int_0^x \exp[-t - Bt^\alpha] dt$. Then $F(x, \alpha, B) = \exp(x + Bx^\alpha) [F(0, \alpha, B) - I(x, \alpha, B)]$. For the calculation of the integral let us develop

the exponential in a Taylor series and integrate one member after the other

$$I(x, \alpha, B) = \int_0^x \sum_{k=0}^{\infty} \sum_{s=0}^k (-1)^k \frac{B^s t^{k+s(\alpha-1)}}{(k-s)! s!} dt =$$

$$= \sum_{k=0}^{\infty} \sum_{s=0}^k (-1)^k \frac{B^s x^{k+s(\alpha-1)+1}}{(k-s)! s! [k+s(\alpha-1)+1]} \quad (22)$$

This series can be transformed so as to make convergence more rapid for α near to 1. We transform the term $1/[k+s(\alpha-1)+1]$ and obtain

$$I(x, \alpha, B) = x \sum_{k=0}^{\infty} \frac{(-x - Bx^\alpha)^k}{(k+1)!} -$$

$$- (\alpha-1) \sum_{k=1}^{\infty} \sum_{s=1}^k (-1)^k \frac{B^s x^{k+s(\alpha-1)+1}}{(k-s)! (s-1)! (k+1) [k+(\alpha-1)s+1]} =$$

$$= x \sum_{k=0}^{\infty} \frac{(-x - Bx^\alpha)^k}{(k+1)!} +$$

$$+ (\alpha-1) Bx^\alpha \sum_{k=0}^{\infty} \sum_{s=0}^k (-1)^k \frac{B^s x^{k+s(\alpha-1)+1}}{(k-s)! s! (k+2) [k+1+\alpha+s(\alpha-1)]} \quad (23)$$

With an analogous transformation of the member $1/[k+1+\alpha+s(\alpha-1)]$ and by its repeating we obtain

$$I(x, \alpha, B) = x \sum_{s=0}^{\infty} (\alpha-1)^s (Bx^\alpha)^s \sum_{k=0}^{\infty} \frac{(-x - Bx^\alpha)^k}{k! \pi [k+1+s+j(\alpha-1)]} =$$

$$= x \left[\frac{1 - \exp(-x - Bx^\alpha)}{x + Bx^\alpha} + \sum_{s=1}^{\infty} (\alpha-1)^s (Bx^\alpha)^s \sum_{k=0}^{\infty} \frac{(-x - Bx^\alpha)^k}{k! \pi [k+1+s+j(\alpha-1)]} \right] \quad (24)$$

The last transformation cannot be used for very small x because of the loss of significant digits in the subtraction $1 - \exp(-x - Bx^\alpha)$. The series converges for all positive x, α, B , because for $\alpha \geq 1$ it has been majorant $x \sum_{s=0}^{\infty} (\alpha-1)^s (Bx^\alpha)^s \sum_{k=0}^{\infty} (x + Bx^\alpha)^k / k! (s+1)^{s+1}$ and for $\alpha \leq 1$ the majorant $x \sum_{s=0}^{\infty} (1/\alpha-1)^s (Bx^\alpha)^s \sum_{k=0}^{\infty} (x + Bx^\alpha)^k / k! (s+1)^{s+1}$ both of which converge for all positive x, α, B . Convergence by s is very rapid for α near to 1, small B and not too large x , thanks to the factor $[(\alpha-1)B]^s$, convergence by k is comparable to the convergence of the series for e^{-x} . For larger values of x convergence is very slow and loss of significant digits occurs in the subtraction $F(0, \alpha, B) - I(x, \alpha, B)$, so that the formula is not suitable for calculation. This formula was applied in the calculation of the function $F(x, 1.04, 0.15)$ on the calculator

SHARP PC-1002 for the values

$$\log_{10}[c_1^b/(1 - c_1^b)] \geq 0.79, \quad \text{i.e. } x \leq 2.641709434.$$

6. In the integral we make the substitution $z = t + Bt^\alpha$, $dz = (1 + \alpha Bt^{\alpha-1}) dt$:

$$\begin{aligned} F(x, \alpha, B) &= \exp(x + Bx^\alpha) \int_x^\infty \exp(-t - Bt^\alpha) dt = \\ &= \exp(x + Bx^\alpha) \int_{x+Bx^\alpha}^\infty f(z) \exp(-z) dz, \end{aligned} \quad (25)$$

where $f(z)$ is a function of the variable z defined parametrically by the equations $f(z) = 1/(1 + \alpha Bt^{\alpha-1})$, $z = t + Bt^\alpha$. We develop the function $f(z)$ in a Taylor series at $z = x + Bx^\alpha$ and integrate member after member $F(x, \alpha, B) = f(x + Bx^\alpha) + \sum_{k=1}^{\infty} (d^k f(z)/dz^k)_{z=x+Bx^\alpha}$. The derivative of the function $f(z)$ is calculated according to the well known formula for the derivative of a parametric function $d/dz = (df/dt)/(dz/dt)$; in this way a parametric expression of the derivative and by repeating this procedure the higher derivatives are obtained. The result is

$$\frac{d^k f}{dz^k} = - \frac{(\alpha - 1) c(1 - c)}{t + \alpha Bt^\alpha} \left(\frac{-(\alpha + 1)}{2(t + \alpha Bt^\alpha)} \right)^{k-1} P_{k-1} \left[\frac{\alpha - 1}{\alpha + 1} (1 - 2c), \left(\frac{\alpha - 1}{\alpha + 1} \right)^2 \right],$$

where $c = 1/(1 + \alpha Bx^{\alpha-1})$, $P_0(u, v) = 1$, $P_k(u, v) = [k + (k + 2)u] P_{k-1}(u, v) + (u^2 - v)$. $\partial P_{k-1}(u, v)/\partial u$. From here $P_1(u, v) = 3u + 1$, $P_2(u, v) = 15u^2 + 10u + 2 - 3v = (5r^2 + s)/3$, $P_3(u, v) = 105u^3 + 105u^2 + (40 - 45v)u + 6 - 19v = (35r^3 + (15r + 4)s)/9$, $P_4(u, v) = 945u^4 + 1260u^3 + (700 - 630v)u^2 + (196 - 504v)u + 24 - 116v + 45v^2 = (105r^4 + (70r^2 + 28r + 8 + 5s)s)/9$, $P_5(u, v) = 10395u^5 + 17325u^4 + (12600 - 9450v)u^3 + (5068 - 10962v)u^2 + (1148 - 4732v + 1575v^2)u + 120 - 776v + 729v^2 = (1155^5 + (1050r^3 + 504r^2 + (224 + 175s)r + 64 + 68s)s)/27$, where $r = 3u + 1$, $s = 1 - 9v = 4(2 - \alpha)$. $(2\alpha - 1)/(\alpha + 1)^2$. The latter expression by means of r and s is numerically more simple, and for this reason it was used in the practical calculation; it also indicates that for $1/2 \leq \alpha \leq 2$, $P_k(u, v) > 0$, so that all derivatives are functions of z with decreasing absolute value. In point $z = x + Bx^\alpha$, $t = x$, so that by substitution we obtain

$$\begin{aligned} F(x, \alpha, B) &= c_0 - \frac{(\alpha - 1) c_0(1 - c_0)}{x + \alpha Bx^\alpha} \sum_{k=0}^{\infty} \left[\frac{-(\alpha - 1)}{2(x + \alpha Bx^\alpha)} \right]^k P_k \left[\frac{\alpha - 1}{\alpha + 1} (1 - 2c_0), \right. \\ &\quad \left. \left(\frac{\alpha - 1}{\alpha + 1} \right)^2 \right], \end{aligned} \quad (26)$$

where $c_0 = 1/(1 + \alpha Bx^{\alpha-1})$. The same result is obtained, if the equation $dc_1(t)/dt = -[k_{12}(t) + k_{21}(t)] [c_1(t) - c_1^b(t)]$ is transformed to the form $c_1(t) = c_1^b(t) - (dc_1(t)/dt)/[k_{12}(t) + k_{21}(t)]$ and solved by iterative procedure with $c_1^{(1)}(t) = c_1^b(t)$. Here $x = (A_2/b_2) \exp(-b_2 t)$, $c_0 = c_1^b(t)$, and t is time.

Because the function $f(z)$ has a singularity at $z = 0$, the radius of convergence of the Taylor series is at most $x + Bx^\alpha$. Thus in our development this series is divergent, but for large x it is semiconvergent. In addition, for $1/2 \leq \alpha \leq 2$, the value of the function is limited by any two

neighbouring partial sums of the semiconvergent series. For α near to 1, $P^k(u, v)$ is near to $k!$. Because $\sum_{k=0}^{\infty} k!(-t)^k$ is an asymptotic development of the function $\varphi(t) = t e^t E_1(t)$, where $E_1(t) = \int_t^{\infty} (e^{-x}/x) dx$, our formula can be rewritten in the form

$$F(x, \alpha, B) = c_0 - \frac{(\alpha - 1) c_0 (1 - c_0)}{x + \alpha B x^\alpha} \left\{ \varphi \left(\frac{2(x + \alpha B x^\alpha)}{\alpha + 1} \right) + \sum_{k=1}^{\infty} \left(\frac{-(\alpha + 1)}{2(x + \alpha B x^\alpha)} \right)^k \left[P_k \left\{ \frac{\alpha - 1}{\alpha + 1} (1 - 2c_0), \left(\frac{\alpha - 1}{\alpha + 1} \right)^2 \right\} - k! \right] \right\}. \quad (27)$$

By this transformation convergence is accelerated and the limits of the applicability of the asymptotic development are increased. More generally the function $\gamma \varphi(\beta \cdot 2(x + \alpha B x^\alpha)/(\alpha + 1))$ may be used instead of the function $\varphi(2(x + \alpha B x^\alpha)/(\alpha + 1))$, where β and γ are suitably selected constants, and $\gamma k!/\beta^k$ is subtracted from $P_k(u, v)$. Selecting $\beta = P_{i+1}(i + 2)/P_{i+2}$, $\gamma = \beta^{i-1} P_{i+1}/(i + 1)!$ and if in addition $P_{i+3} \geq \gamma(i + 3)!/\beta^{i+3}$, then the value of the function $F(x, \alpha, B)$ lies between the i -th and $(i - 1)$ st partial sum of the series. By this selection of the values β and γ for two neighbouring values of i we obtain the best upper and lower guess for the function $F(x, \alpha, B)$. For a practical calculation we have selected for β the largest value $\beta \leq P_{i+1}(i + 2)/P_{i+2}$ for which $2\beta(x + \alpha B x^\alpha)/(\alpha + 1)$ is an argument of the function $\varphi(x)$ in tables⁸, in order to avoid table interpolation: γ is given by the formula $\gamma = \beta^{i+1} P_{i+1}/(i + 1)!$. In this way the limits of the integral are increased insignificantly; for $P_{i+2} > \gamma(i + 2)!/\beta^{i+2}$ the integral may not lie between the i -th and $(i - 1)$ st partial sum of the series, hence the condition $\beta \leq P_{i+1}(i + 2)/P_{i+2}$. The asymptotic development according to this paragraph has been used for the calculation of the function $F(x, 1.04, 0.15)$ on the calculator SHARP PC-1002 for values $\log_{10}(c_1^b/(1 - c_1^b)) \leq 0.80$. A control calculation for the value of the argument 0.79 (*i.e.* $x = 2.641709434$), using the last transformation with $i = 2$ and $i = 3$ yielded limits of the value of F differing by $4 \cdot 10^{-6}$; the value calculated according to paragraph 5 lay within these limits.

7. If the combination of the methods of paragraphs 5 and 6 does not lead to the required accuracy in the whole range of x , then

$$F(x, \alpha, B) = e^{x + B x^\alpha} \int_x^{x_0} e^{-t - B t^\alpha} dt + e^{-q} F(x_0, \alpha, B), \quad (28)$$

where $q = x_0 + B x_0^\alpha - x - B x^\alpha$, $x_0 > x$. Then

$$\exp(x + B x^\alpha) \int_x^{x_0} e^{-t - B t^\alpha} dt = \int_{x + B x^\alpha}^{x_0 + B x_0^\alpha} f(z) \exp(-z + x + B x^\alpha) dz, \quad (29)$$

where $f(z)$ is the parametric function defined in paragraph 6. Developing the function $f(z)$ in a Taylor series at $z = x + B x^\alpha$ we obtain

$$F(x, \alpha, B) = e^{-q} \left\{ c_0 I_0(q) - \frac{(\alpha - 1) c_0 (1 - c_0)}{x + \alpha B x^\alpha} \sum_{k=0}^{\infty} I_{k+1}(q) \left(\frac{-(\alpha + 1)}{2(x + \alpha B x^\alpha)} \right)^k \cdot P_k \left[\frac{\alpha - 1}{\alpha + 1} (1 - 2c_0), \left(\frac{\alpha - 1}{\alpha + 1} \right)^2 \right] + F(x_0, \alpha, B) \right\}. \quad (30)$$

Here $I_k(\varrho) = (e^\varrho/k!) \int_0^\varrho t^k e^{-t} dt = e^\varrho - \sum_{s=0}^k \varrho^s/s!$ and the other symbols have the same meaning as in paragraph 6. The expression $I_k(\varrho)$ has to be calculated by means of a Taylor series development of the function e^ϱ , or possibly by means of the recurrent formula $I_{k-1}(\varrho) = \varrho^k/k! + I_k(\varrho)$, in case that there is danger of loss of significant digits in consequence of direct subtraction. In calculating by this procedure we start from values where the required accuracy can be reached from the asymptotic development of paragraph 6. The value of x is then decreased in suitably selected steps, with the old value of x always becoming the new x_0 . In this way we proceed until we reach the value of x for which the series from paragraph 5 is applicable. By suitable selection of the steps, an arbitrary degree of accuracy may be reached.

8. For the Eyring relation $k_{12} = (kT/h) \exp [\Delta S_1^\ddagger/R - \Delta H_1^\ddagger/(RT)]$, $k_{21} = (kT/h) \exp . [\Delta S_2^\ddagger/R - \Delta H_2^\ddagger/(RT)]$. Let us set $1/T = at$, $A_1 = (k/ha) \exp [\Delta S_1^\ddagger/R]$, $A_2 = (k/ha) \exp . (\Delta S_2^\ddagger/R)$, $b_1 = a \Delta H_1^\ddagger/R$, $b_2 = a \Delta H_2^\ddagger/R$, $\alpha = b_1/b_2 = \Delta H/\Delta H_2^\ddagger$. It should be noted that the values of A_1 and A_2 are of the order of 10^{17} . Then

$$c_1(t) = \exp [A_1 E_1(b_1 t) + A_2 E_1(b_2 t)] \int_0^{b_2 t} (A_2/x) \exp [-x - A_1 E_1(\alpha x) - A_2 E_1(x)] dx . \quad (31)$$

We make the substitution $z = A_1 E_1(\alpha x) + A_2 E_1(x)$,

$$dz = -(A_1 e^{-\alpha x} + A_2 e^{-x}) x^{-1} dx :$$

$$c_1(t) = \exp [A_1 E_1(b_1 t) + A_2 E_1(b_2 t)] \int_v^\infty f(z) e^{-z} dz ; \quad (32)$$

where $v = A_1 E_1(b_1 t) + A_2 E_1(b_2 t)$ and the function $f(z)$ is defined parametrically by the relations $f(z) = A_2 e^{-x}/(A_1 e^{-\alpha x} + A_2 e^{-x})$, $z = A_1 E_1(\alpha x) + A_2 E_1(x)$. The function $f(z)$ is developed in Taylor series at $z = A_1 E_1(b_1 t) + A_2 E_1(b_2 t)$, i.e. $x = b_2 t$. Applying the relation $dz/dx = -(A_1 e^{-\alpha x} + A_2 e^{-x})/x$ we obtain for the derivatives expressions analogous to those of paragraph 6. By integration *per partes* with an upper limit ∞ we obtain a semiconvergent asymptotic series applicable for small t . As soon as this series ceases to yield the required accuracy, we integrate *per partes* similarly as in paragraph 7, thus gradually increasing the value of t . For very large t the calculation would require too many steps; we then make use of the fact that $\int_{b_2 t}^\infty (A_2/x) \exp [-x - A_1 E_1(\alpha x) - A_2 E_1(x)] dx \approx (A_2/b_2 t) \exp (-b_2 t)$ for very large t , or that for this integral an asymptotic development in the form of a power series in the variables t^{-1} , $\exp(-b_1 t)$ and $\exp(-b_2 t)$ may be obtained so that $\exp [-A_1 E_1(\alpha x) - A_2 E_1(x)]$ is developed in Taylor series, the functions $E_1(\alpha x)$ and $E_1(x)$ are substituted by asymptotic developments, we integrate *per partes* and in the result the functions $E_1(\alpha x)$ and $E_1(x)$ are once more substituted by asymptotic developments. The value of the integral in the limits $(b_2 t', b_2 t)$ is then obtained by subtracting the values in the limits $(b_2 t', \infty)$ and $(b_2 t, \infty)$; t' is selected as the largest of the t values for which the function $c_1(t)$ has been calculated by step integration.

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