$$(2 + \beta_{33}m_3')\left[m_3 \ln \frac{m_3}{m_3'} - (m_3 - m_3')\right] + \beta_{22}^0 m_2^2/2 + \beta_{222}^0 m_2^3/3 + \beta_{2222}^0 m_2^4/8 + \ldots \quad (15)$$

If the second and third terms are large, we should limit the expansion to the following terms. For albumin solutions with sodium chloride, however, these terms are so small that it is convenient to expand the logarithms, to give

$$\frac{PV_m}{RT} = m_2 + \frac{z_2^2 m_2^2}{4m_3} + \frac{z_2^4 m_2^4}{32m_3^3} + \ldots - (2 + \beta_{33}m_3')\left(\frac{(m_3 - m_3')^2}{2m_3} + \frac{(m_3 - m_3')^3}{3m_3^2}\right) + \beta_{22}^0 m_2^2/2 + \beta_{222}^0 m_2^3/3 + \beta_{2222}^0 m_2^4/8 + \ldots \quad (16)$$

If we compare this with the equation

$$PV_m/RT = m_2(1 + B_2 w_2 + B_{22}^0 w_2^2) \quad (17)$$

and a similar expansion of equation 1 to give

$$b_{23}w_2 = -\left(\frac{m_3 - m_3'}{m_3}\right) - \left(\frac{m_3 - m_3'}{m_3}\right)^2/2 \quad (18)$$

we find that

$$B_2^0\left(\frac{w_2}{m_2}\right) = \frac{z_2^2}{4m_3} - (2 + \beta_{33}m_3')\frac{b_{23}^2 m_3}{2}\left(\frac{w_2}{m_2}\right)^2 + \frac{\beta_{22}^0}{2} \quad (19)$$

$$B_{22}^0\left(\frac{w_2}{m_2}\right)^2 = +(2 + \beta_{33}m_3')\frac{b_{23}^3 m_3}{6}\left(\frac{w_2}{m_2}\right)^3 \frac{\beta_{222}^0}{3} \quad (20)$$

Combining these equations with equation 4, we obtain, for $m_3 = 0.15$

$$\beta_{22}^0 = 575 - 34z_2 - 3.33z_2^2 + 230 = 805 - 34z_2 - 3.33z_2^2 \quad (21)$$

$$\beta_{222}^0 = 119{,}000 - 7{,}000z_2 + 3400 = 122{,}400 - 7000z_2 \quad (22)$$

The term arising from b_{23} is almost a third of the total at $z_2 = 0$ for β_{22}^0, but only a thirtieth for β_{222}^0, and the Donnan term contributes nothing to β_{222}^0. Therefore β_{222}^0 is determined to a good approximation from B_{22}^0 alone.

Recalling that β_{23} is nearly inversely proportional to m_3, we may write

$$\beta_2 = \ln \gamma_2 = \ln \gamma_2^0 + \beta_{23}^0 m_3 \ln m_3 + \beta_{22}^0 m_2 + \beta_{222}^0 m_2^2/2 \quad (23)$$

in which $\ln \gamma_2^0$ is a constant depending upon the choice of standard state. With the values of the parameters given above, we obtain for this sample of crystallized bovine serum albumin (ACB-2) in aqueous sodium chloride solutions at 25°

$$\ln \gamma_2 = \ln \gamma_2^0 - 8.0 \ln m_3 + (805 - 34z_2 - 3.33z_2^2)m_2 + (61{,}700 - 3500z_2)m_2^2 \quad (24)$$

This equation should be valid over the ranges of m_2 from 0 to 250, m_3 from 0.1 to 0.2 and z_2 from 0 to −13.

Summary

The osmotic pressure and the distribution of salt across a semipermeable membrane have been measured for crystallized bovine serum albumin up to concentrations of 25% in 0.15 *M* aqueous sodium chloride at *p*H 5.4 to 7.2 and 25°.

Although the molecular weight appears to be the same, the protein–electrolyte and protein–protein interactions were slightly different from those of the sample previously studied.

The equations for osmotic equilibria have been extended to higher approximations.

Analytical expressions have been derived for the measured quantities, for the interactions and for the activity coefficient as a function of the concentration of albumin and of salt.

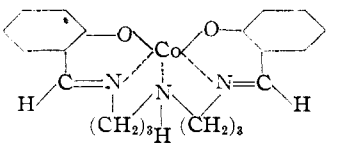
CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 27, 1946

[CONTRIBUTED BY THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Oxygen-Carrying Synthetic Chelate Compounds. VI. Equilibrium in Solution

BY O. L. HARLE[1] AND M. CALVIN

In the previous paper of this series[2] the equilibrium between oxygen and the solid chelates was described. These were primarily on compounds of Type I,[3] that is, chelate compounds derived from the Schiff base formed by salicylaldehyde or its derivatives with ethylenediamine. The present paper contains the results of equilibrium measurements on chelate compounds in solution. The chelates used in this study were primarily of Type II[3]; that is, compounds derived from the Schiff base formed by salicylaldehyde or its derivatives with γ,γ'-diaminodipropylamine.



Type II.

The reason for the lack of overlap between the measurements on the solids and those on solutions is primarily the fact that: (1) the pressures over solutions of Type I are very low, a few millimeters or less, so that the vapor pressure of the solvent interferes, making such measurement somewhat more difficult than those on solutions of Type II where the pressure range is relatively high; and (2) the pressures over the solids of Type II are in general above one atmosphere and the

(1) Abstracted from the thesis submitted in 1944 by O. L. Harle to the Graduate School of the University of California at Berkeley in partial fulfillment of the requirements for the Ph.D. degree.

(2) E. W. Hughes, W. K. Wilmarth and M. Calvin, THIS JOURNAL, **68**, 2273 (1946).

(3) Calvin, Bailes and Wilmarth, *ibid.*, **68**, 2254 (1946).

approach to equilibrium quite slow, making these also the more laborious to obtain. We hope, of course, to go into these ranges as time permits.

Experimental

The apparatus used is shown in Fig. 1. It consists of an evacuable system, with mercury manometer, gas buret and reaction vessel. The tube serving the reaction vessel is equipped with a glass spring (F) to allow shaking of the vessel. The manometer is equipped with a reservoir (K) so that the mercury level in the dead arm will show little change as the level changes in the arm open to the system. The dead arm contains a constriction to prevent rapid flow of mercury into or out of that arm. A two-way stopcock (5), one way open to the room, serves in introduction of oxygen.

The volumes of various sections of the apparatus were measured by expansion of gas of measured pressure and volume through the system, with subsequent remeasurement of pressure and volume. The volume of the system, with one of the two reaction vessels of almost identical design which were used, is 99.0 cc.; with the other, the volume is 114.3 cc.

During the course of measurements, the temperature of the reaction vessel was held within one degree of the desired level by a flow of liquid through the jacket surrounding the vessel. A thermometer immersed in the contents of the jacket was used to indicate the reaction temperature. The liquid was introduced from a large reservoir, and withdrawn after its course through the jacket by an aspirator to the drain. Manual control of the temperature was maintained by a pinchcock which allows variable rates of flow of liquid into the jacket at its lower part (H, Fig. 1).

In making measurements, the whole system was evacuated, and the solution, made up in the vessel after evacuation, was shaken under constant vacuum-pumping for ten minutes. Then, with the shaker stopped, oxygen was admitted at the desired pressure until the buret was almost filled. The rate of diffusion of gases into these solvents when not shaken is negligible. After recording initial pressure, temperature, and volume, the shaker was started. The mercury in the buret was used to maintain constant pressure. Time-scaled volumes recorded in the course of the process gave total oxygen absorption rate (Fig. 3). When the rate became zero and remained so for ten minutes, equilibrium was assumed. The volume recorded at that time gave the total oxygen uptake of the solution. Twenty minutes was usually required for a complete measurement, the absorption being almost finished in the first four to ten minutes. Pressure and temperature were always constant throughout a measurement. Fifty-cc. samples always were used. This same procedure was followed to determine the solubility of oxygen in the pure solvent. Linde U.S.P. oxygen was used, without drying or purifying.

Precision was found to be best for absorptions greater than 15 cc. at pressures above 15 cm. These conditions were usually satisfied in measurements made between 15 and 50 cm. of pressure. At a pressure of 20 cm., with 50-cc. oxygen uptake, precision was about 1%. At 60 cm. of pressure, with 15 cc. oxygen, uptake, precision was about 3–5%. At pressures below 5 cm. and large volumes of oxygen uptake, precision was not better than 5%. These estimates are made from variations in comparable measurements (Table I).

Difficulty was encountered in bringing the chelates into solution. They are not very soluble in the solvents used, and the rate of solution, even of thoroughly powdered samples, is small. Furthermore, the solution must be made in the complete absence of oxygen. The apparatus used is more closely shown in Fig. 2. The chelate (0.5 or 1.0 mmol) was placed in glass tube (A) containing a few lead shot (J) at the bottom, and a plunger (I) sunk below the bulk of the chelate powder. The plunger was fixed by wire to the glass hook (B) from which the tube was suspended by a steel ring. The solvent, previously exhausted of gases, was in the vessel below the tube. The whole was

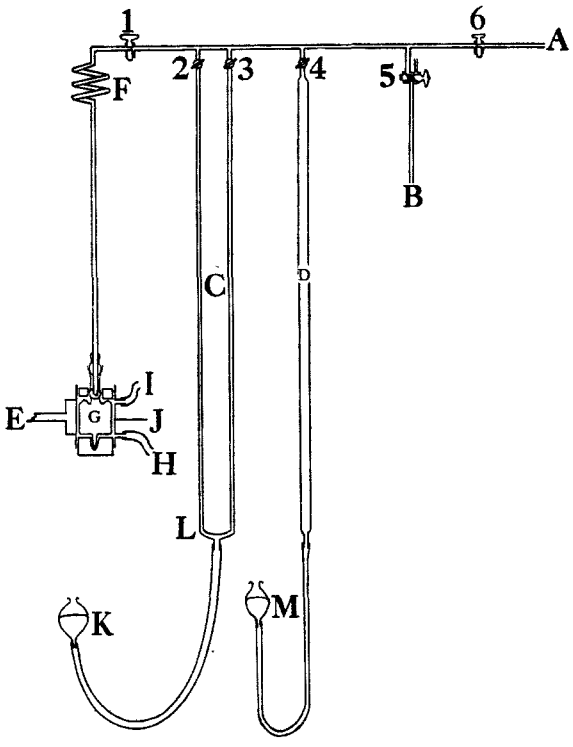


Fig. 1.—Diagram of apparatus: A, to liquid air trap, mercury diffusion pump, and McLeod gage; B, to oxygen tank; C, mercury manometer; D, 100 ml. gas buret; E, to shaker; F, glass spring; G, reaction vessel; H, inlet from constant-temperature bath; I, outlet to drain; J, constant-temperature jacket; K, manometer reservoir; L, dead-arm constriction; M, buret reservoir.

at this stage evacuated, and the temperature jacket filled with boiling water. A small magnet was applied externally to free the steel ring from the hook, and the falling of the tube drew the plunger, pulling out most of the chelate powder. Vigorous shaking stirred the mixture and caused the lead shot to carom about, freeing the remainder of the chelate from the tube. All this was necessary because the powder, if wet in the tube, set to a virtually insoluble concretum. The solution was then brought to the reaction temperature, and the measurement was made. The solutions were usually 0.01 *M* or 0.20 *M*; even so, an activity in oxygenation only 80% that of 0.01 *M* solutions indicated that 0.02 *M* solutions at −10° gave about 20% precipitation of solid chelate from solution.

The solvents used (quinoline, ethyl benzoate and α-methylnaphthalene) were chosen on the basis of their character as acids or bases, and their expected tendency to form complexes with group VIII metals. The quinoline and ethyl benzoate (both Eastman Kodak Co. chemicals) were used, after one distillation in the case of quinoline, and directly, as received, in the case of the ethyl benzoate. Due to limited supplies, however, the solvent was used over and over again, each time after distillation of the previous reaction solutions. In both cases, results obtained in the solvent thus many times redistilled were in good agreement with all previous results, so it is assumed that impurities are probably not present in significant amounts, or, if present, are uniformly brought over in the distillations. This would apply to no less than fifteen consecutive redistillations of the quinoline, and fourof the ethyl benzoate. The α-methylnaphthalene was adsorption-extracted twice with Nuchar-OO, steam distilled, and finally distilled at 14 mm. of pressure and between 111 and 112°, through a fifteen-plate bubble-plate column.

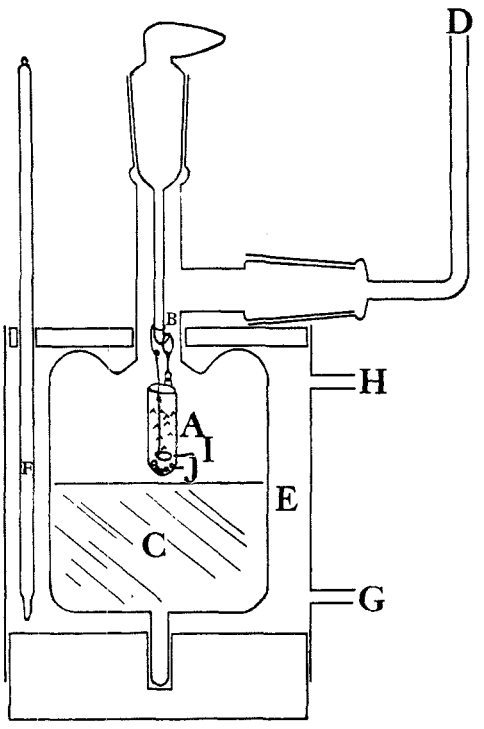


Fig. 2.—Diagram of the reaction vessel: A, tube holding solid chelate; B, hook supporting tube A; C, solvent; D, to measuring system; E, constant-temperature bath; F, thermometer; G, bath inlet; H, bath outlet; I, plunger immersed in solid chelate; J, lead shot.

Enough was available that recovery of this solvent was unnecessary.

Solubility of oxygen in all three solvents was measured by the method given above, and was found to be 3.90 cc. of oxygen/50 cc. of quinoline, independent of pressure and temperature over the ranges 5–60 cm. and 0–30°, respectively.[4] In ethyl benzoate, measurements were made only at 0°, for a pressure range 5–60 cm. The solubility so measured was 6.47 cc. of oxygen/50 cc. of ethyl benzoate. This solubility appeared to have a large temperature dependency, the amount of oxygen dissolved rising sharply if the temperature were allowed to drift to −2°. The solubility of oxygen in α-methylnaphthalene measured only at 0° was found to be 5.35 cc./50 cc. of α-methylnaphthalene. This value applies over the pressure range 5–60 cm. The oxygen volume is measured in each case at room temperature, 22–24° for these solubilities.

The greatest reason for the choice of these particular solvents was their low vapor pressures and high viscosities. Quinoline boils at 237°, ethyl benzoate at 211°, and α-methylnaphthalene at 240°, so that the solvent vapor pressure can be neglected at the temperatures of these measurements, usually 0° and never higher than 30°. The high viscosity prevented rapid diffusion of oxygen into the solutions while the shaker was not in operation. It was found that degassed quinoline and α-methylnaphthalene solutions could stand under oxygen at 20 cm. pressure for fifteen minutes with no perceptible absorption of oxygen. Ethyl benzoate, a somewhat mobile liquid, required more care; two or three minutes of standing under the stated conditions gave an observable oxygen uptake. The oxygenation of solutions is always strongly indicated by a color change from strong yellow to an almost opaquely intense red.

(4) Since this solubility is measured in units of vol. of gas/vol. of solvent, the solubility in moles of gas/mole solvent is directly proportional to the pressure.

The chelates studied in this survey may be listed

(a) Co-3-x-sal-prtr, where x might be Cl, F, $-OC_2H_5$, $-NO_2$, or —H (Type II)
(b) Co-sal-en (Type I)
(c) Co-NH-benz-en

The chelates were all easily brought into solution as described above. Quinoline, the first solvent tried, was the least desirable in this respect, that solubilities of all chelates appeared to be least and slowest in it. But since a large part of the work had been done before the other solvents were investigated, quinoline was used for all experiments except the experiments designed specifically to check solvent effect upon the oxygenation reaction. In all experiments except those done at 0 and 30° with Co-3-Cl-sal-prtr in quinoline, the concentration of chelate was 0.01 *M* (0.500 mmole in 50 cc. of solvent). The set mentioned was performed with 0.02 *M* chelate solutions (1.000 mmole in 50 cc. of quinoline).

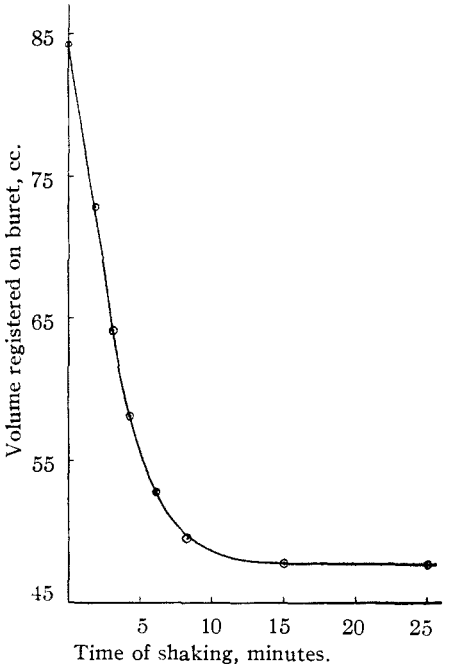


Fig. 3.—Plot of oxygen volume measured at 21° *vs.* time of shaking for a typical oxygenation reaction, illustrating the reaching of zero rate of uptake as a criterion of equilibrium. Reaction was at 0° in quinoline. Chelate used was Co-3-Cl-sal-prtr, 0.020 *M* oxygen, was at 35.1 cm. of pressure.

The oxygenation reaction is found to be almost completely reversible at 0°; that is, irreversible oxidation of chelate is negligible. One sample of chelate, which gave initially an oxygen uptake of 0.618 mmole/mmole of chelate at 0° and a 37.78 cm. pressure of oxygen, when deoxygenated for one hundred and eighty-five minutes after three-hundred minutes of exposure to oxygen at the stated pressure gave an oxygen uptake on titration of 0.552 mmole oxygen/mmole chelate; it was thus at least 89.5% as active as the original sample. Another sample, 1 mmole of the same chelate (Co-3-Cl-sal-prtr), in 50 cc. of quinoline, gave at 0° and 76.0 cm. of pressure of oxygen an uptake of 0.721 mmole oxygen/mmole of chelate. The exposure to oxygen was twenty minutes. After four hours of deoxygenation, the same sample took up 0.712 mmole oxygen/mmole of chelate, the loss of activity being 1.1%. Deoxygenation is accomplished simply by shaking the oxygenated chelate solution, at 0°, under high vacuum.

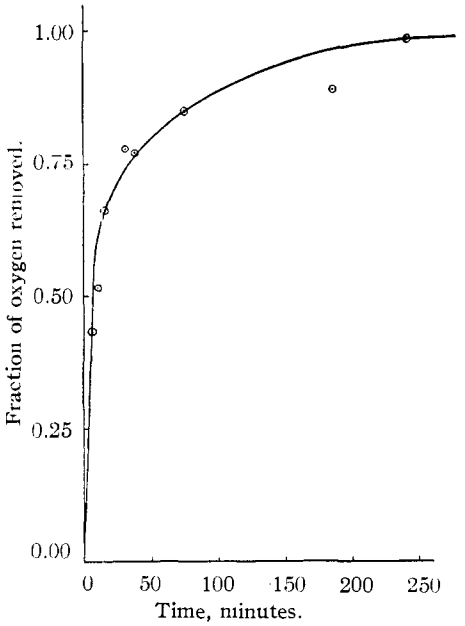


Fig. 4.—Rate of deoxygenation of chelate solutions. Various samples, during the course of examining the oxygenation at 0° of Co-3-Cl-sal-prtr, were deoxygenated for the times here shown, then reoxygenated. This plot shows fraction of original oxygen absorbed by reoxygenation of the partially deoxygenated solutions at the original conditions, in most cases 37.78 cm. of oxygen pressure.

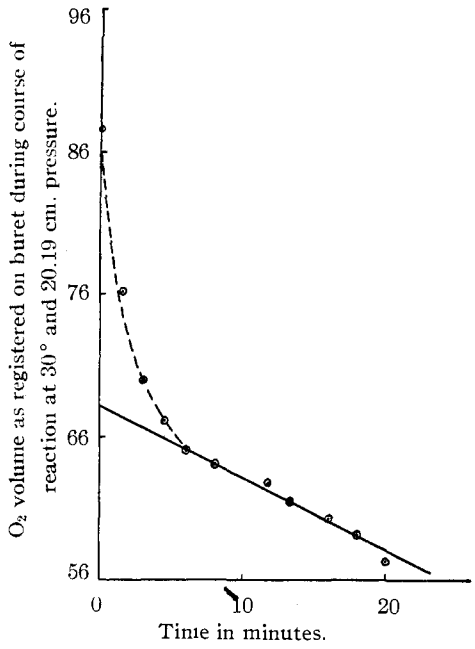


Fig. 5.—Plot of data for 30° and 20.19 cm. to illustrate validity of linear rate extrapolation for the purpose of separate estimation of reversible and irreversible reaction with oxygen: Co-3-Cl-sal-prtr in quinoline.

The rate of deoxygenation is low if complete deoxygenation is desired; by the titration method outlined in the above experiment, it was found that for a sample of chelate which in quinoline at 0°, and under a pressure of 37.78 cm. of oxygen, absorbed 0.618 mmole oxygen per mmole of chelate initially, the absorption was only 0.410 mmole oxygen/mmole of chelate, or 66.4% of the original, after fifteen minutes of deoxygenation (Fig. 4). It was thus impractical to use the same sample of chelate for many successive experiments, since complete deoxygenation requires of the order of four hours. In all these tests, the chelate was Co-3-Cl-sal-prtr. The reversibility of the oxygenation of this same chelate in ethyl benzoate was tested at 0°; a sample which absorbed 0.502 mmole oxygen/mmole of chelate initially, reabsorbed after three hours of deoxygenation 0.487 mmole oxygen/mmole of chelate; the activity was 97.2% of the original. In all subsequent experiments, a new sample of chelate was dissolved for each measurement, since deoxygenation requires so long a time.

At higher temperatures (above 10°), the uptake of oxygen is far from reversible, if exposure of the chelate solution to oxygen is for any great length of time. It is found, in fact, that in oxygenation measurements made as described above, for the case of chelate solutions at 30°, the rate of oxygen uptake never becomes zero. After the large initial uptake in the first five minutes of exposure of chelate solution to oxygen, the rate merely falls off to a small constant value, the uptake becoming, for a relatively long period (fifteen to twenty minutes) approximately linear with time. This is illustrated in Fig. 5 where the buret readings at various times over a period of twenty minutes are plotted against time, for an experiment performed at 30° upon 1.000 mmole of chelate dissolved in 50 cc. of quinoline under oxygen pressure of 20.19 cm., the chelate being Co-3-sal-prtr. As is seen, all points taken after six minutes fall approximately on a straight line. In measurements made at these higher temperatures, the value of the truly reversible oxygenation is obtained by extrapolating this constant-rate uptake to zero time, and assuming that it represents the rate of irreversible oxidation. Then its intercept on the zero-time axis represents the endpoint of the reversible oxygenation, and can be subtracted from the initial volume to obtain the volume of oxygen reversibly taken up. This procedure was applied in all measurements herein given which were made at 20 and 30°; at the lower temperatures, the rate of irreversible oxidation was found to be nil. A certain error is involved here: it is true that the rate of irreversible oxidation will not reach its constant value until a steady-state oxygen concentration is built up in the solution by diffusion. Since it requires four minutes of shaking to saturate the solvent alone with oxygen, it may be assumed that the initial rate of irreversible oxidation is less than that finally attained, and that, in fact, the true intercept of this rate-curve on the axis of zero-time should be lower, and the indicated amount of reversible oxygenation larger than is obtained by the linear extrapolation. This error has not been accounted for, due to lack of precise knowledge of the shape of the rate-curve at low values of time.

Results

It is now desirable to indicate what data have been taken. These are presented in graphic form, with some sample tables. An arbitrary function

$$F = \frac{\text{mmole of oxygen uptake}}{\text{mmole of chelate dissolved}}$$

is the dependent variable in all cases.

Diagram IV gives the pressure and temperature dependency of F for Co-3-Cl-sal-prtr in quinoline. Table I gives the total data from which curve II of Fig. 6 was made.

Figure 7 exhibits the general independence of F with respect to chelate concentration for Co-3-Cl-sal-prtr at 0° and various pressures, in quinoline solution.

TABLE I

TEMPERATURE 0°

(1.000 mmole of Co-3-Cl-sal-prtr in 50 cc. quinoline)

O_2 press., cm.	Values of F (as defined) from various experiments	Average F
76.0	0.721, 0.712	0.717
60.44	.707, .696, 0.699, 0.731	.708
49.94	.679	.679
41.53	.648	.648
37.66	.643	.643
35.10	.625	.625
30.32	.598	.598
27.47	.602	.602
25.17	.577	.577
20.19	.568, .559, .556	
	.568, .579, .548, .550	.561
12.95	.510, .498, .532, .498	.510
5.94	.428, .443	.436
3.21	.355	.355

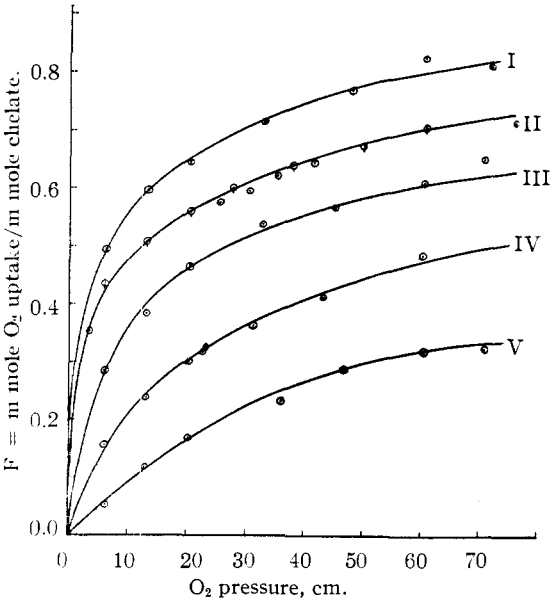


Fig. 6.—Variation of oxygenation with oxygen pressure at five temperatures, in quinoline. Chelate is Co-3-Cl-sal-prtr: I, −10°; II, 0°; III, 10°; IV, 20°; V, 30°.

Substituent effect upon F for Co-3-X-sal-prtr (X = Cl, F, —NO_2, —H, and —OC_2H_5) at 0° in quinoline is demonstrated in Fig. 8.

Solvent effect upon F at 0° for the cases of ethyl benzoate and α-methylnaphthalene is drawn from comparison with the data of Table I, as presented in Fig. 9.

Some fragmentary experimentation done with other chelates should also be mentioned. In the case of Co-sal-en, the so-called parent diamine, which was the cobalt compound in which reversible oxygenation (of the solid) was first observed, three measurements of F were made for 0.0100 M solutions of the chelate in quinoline at 0°. At a pressure of 11.02 cm. of oxygen, the oxygen uptake was 4.20 cc. (measured at 23° room temperature). The solubility of oxygen in quinoline is

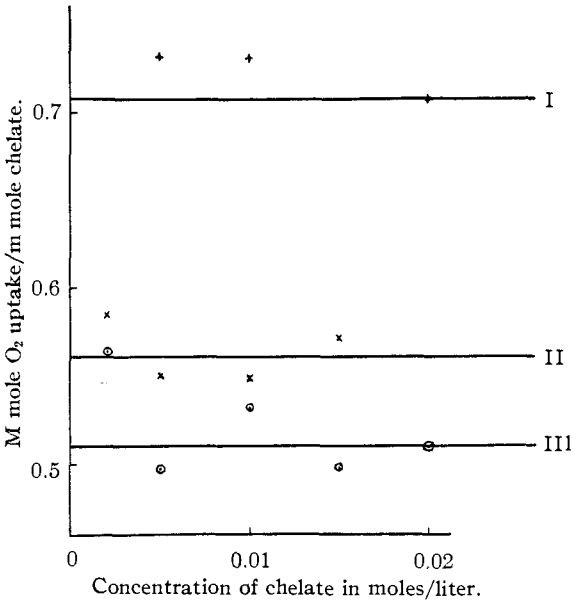


Fig. 7.—Dependence of degree of oxygenation on chelate concentration: Co-3Cl-sal-prtr in quinoline at 0°: I, 60.44 cm. O_2 pressure (+); II, 20.19 cm. O_2 pressure (×); III, 12.95 cm. O_2 pressure (⊙).

3.90 cc. Since the solution remained at its original dark orange color, and no further change in oxygenation was observed even after ten hours of shaking, it is assumed that the value of F is approximately zero. At a pressure of 69.30 cm. of

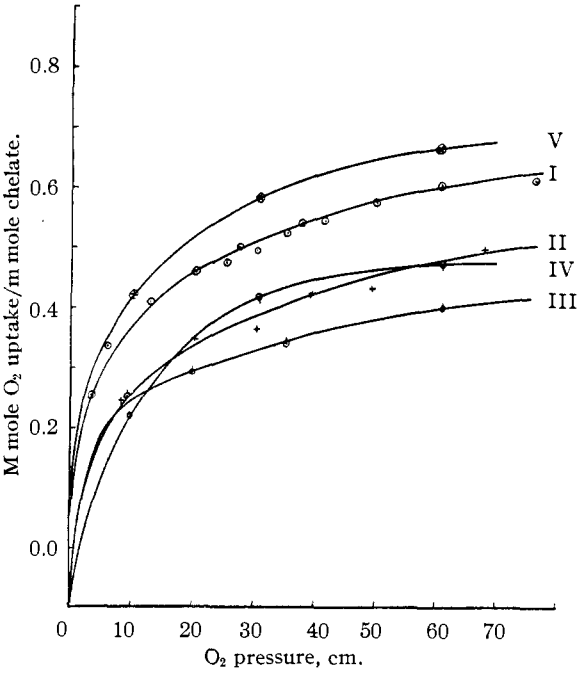


Fig. 8.—Effect of substituents in the 3-position of the salicylaldehyde residue upon the oxygenation at 0° in quinoline: I, chlorine; II, fluorine; III, nitro; IV, hydrogen; V, ethoxy.

oxygen, F has a value of 0.122. The color of the solution becomes clear scarlet under these conditions. If, however, 3.1 cc. (approximately 38 mmoles) of pyridine be added, the value of F at an oxygen pressure of 69.30 cm. (Hg) becomes 0.478. The value of maximum oxygenation of the solid chelate is 0.500 mole of O_2/mole of chelate. No solid was precipitated from this solution, as has been reported to happen in oxygenated pyridine solutions of Co-sal-en.[6] The solution became, upon oxygenation to this degree, an almost opaquely intense red.

All chelates used were either prepared by Dr. R. H. Bailes, or prepared according to his methods.[5] The purity of the substances could not usually be checked except by analysis. In the case of the chelate most often used, Co-3-Cl-sal-prtr, four different preparations were used in the course of this work, and all gave the same values of F at 12.95 cm., 20.19 cm. and 60.44 cm. of pressure of oxygen, at 0° in 0.0200 M solution.

Discussion

In the analysis of the data given in Figs. 6–9, it is desirable to obtain equilibrium equations corresponding to definite chemical reactions between dissolved chelate and oxygen, in order that thermodynamic quantities relating to the reactions may be derived.

It was found that neither the equation

$$2Ch + O_2 = Ch_2O_2 \quad K = [Ch_2O_2]/[Ch]^2P_{O_2}$$

which might be considered from analogy with the stoichiometry of the reaction of oxygen with solid type I chelates, nor

$$Ch + O_2 = ChO_2 \quad K' = [ChO_2]/[Ch]P_{O_2}$$

similarly related to the solid phase reaction of type II chelates with oxygen, alone satisfactorily reproduces the experimental data. (In these and subsequent equations, Ch represents the single chelate molecule.) Furthermore, neither of these equations, taken separately, could be made to fit the data by including the possibility of the following dimerization equilibria

$$2Ch = Ch_2$$
$$2ChO_2 = Ch_2(O_2)_2$$

However, of the many possible forms of two-stage equilibria represented by combinations of the steps illustrated in the equations given above, all that were tried fit the data satisfactorily. In particular, the systems represented by

$$\text{I} \begin{cases} 2Ch + O_2 = Ch_2O_2 & K_1 = [Ch_2O_2]/[Ch]^2P_{O_2} \\ Ch + O_2 = ChO_2 & K_2 = [ChO_2]/[Ch]P_{O_2} \end{cases}$$

involving only single chelate molecules and single oxygen complexes, and

$$\text{II} \begin{cases} Ch_2 + O_2 = Ch_2O_2 & K_3 = [Ch_2O_2]/[Ch_2]P_{O_2} \\ Ch_2O_2 + O_2 = Ch_2(O_2)_2 & K_4 = [Ch_2(O_2)_2]/[Ch_2O_2]P_{O_2} \end{cases}$$

involving only dimerized chelate molecules and dimerized oxygen complexes, both reproduced the data of Fig. 6 and yielded credible thermodynamic

(5) Paper VII of this series, forthcoming.

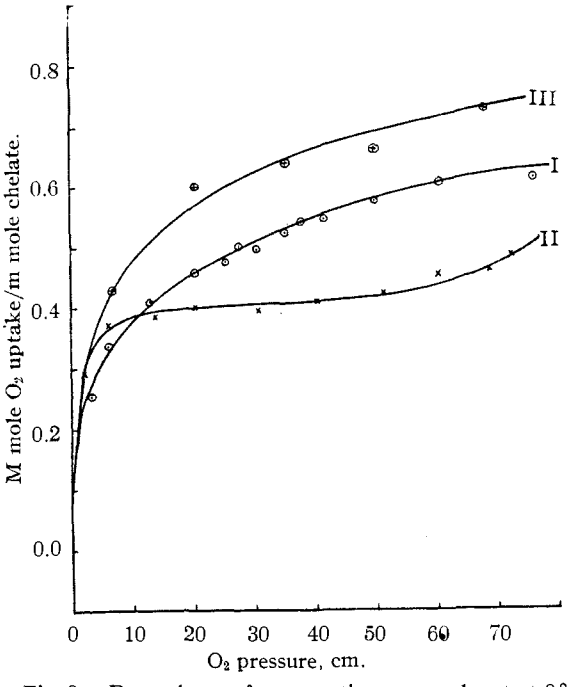


Fig. 9.—Dependence of oxygenation upon solvent at 0°: chelate: Co-3-Cl-sal-prtr; I, quinoline; II, ethyl benzoate; III, α-methylnaphthalene.

quantities as calculated from the values of the equilibrium constants (Table II). The two systems were used separately in calculation. The fact that the dimerization equilibrium may be also in the range measurable by these methods is suggested by the large curvature of the plot of log K *vs.* $(1/T)$ for the first step of both scheme I and scheme II (Fig. 10).

TABLE II

Temp., °C.	Equilibrium constants K_1	K_2	K_3	K_4	F at chosen O_2 pressures 6 cm.	20 cm.	60 cm.
	5300	14	..	..	0.509	0.662	0.813 (72 cm.)
−10	..	...	84	1.8	.496	.643	.786 (72 cm.)
	Observed				.497	.649	.814 (72 cm.)
	1900	7.6	..	..	.441	.580	.708
0	..	...	53	0.91	.438	.565	.700
	Observed				.436	.561	.708
	680	2.7	..	..	.281	.449	.606
10	..	...	15	0.53	.289	.469	.611
	Observed				.285	.467	.614
	170	1.2	..	..	.152	.312	.493
20	..	...	5.6	0.21	.157	.319	.476
	Observed				.157	.302	.487
	15	0.53	..	..	.054	.150	.321
30	..	...	1.5	0.15	.055	.153	.318
	Observed				.054	.170	.321

$\Delta H_1 = -15$ kcal. $\quad \Delta H_2 = -14$ kcal.
$\Delta F_1 = -4.1$ kcal. $\quad \Delta F_2 = -1.1$ kcal.
$\Delta S_1 = -40$ e. u. $\quad \Delta S_2 = -47$ e. u.
$\Delta H_3 = -10.5$ kcal. $\quad \Delta H_4 = -10$ kcal.
$\Delta F_3 = -2.2$ kcal. $\quad \Delta F_4 = 0.05$ kcal.
$\Delta S_3 = -30$ e. u. $\quad \Delta S_4 = -37$ e. u.

The values of F for scheme I are obtained from the equations

$$F = P_{O_2} \frac{K_1[Ch] + K_2}{1 + 2K_1[Ch]P_{O_2} + K_2P_{O_2}}$$

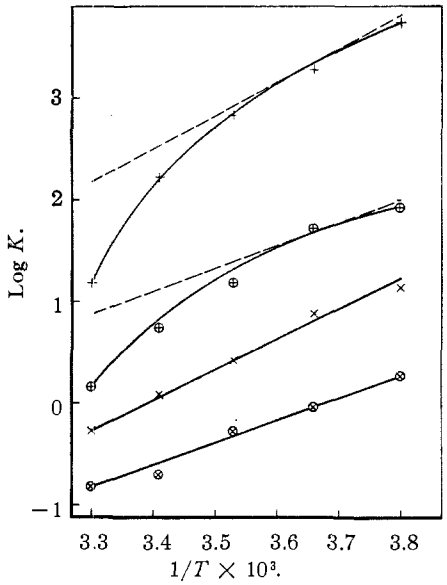


Fig. 10.—Log_{10} K as a function of $1/T$: +, K_1; ×, K_2; ⊕, K_3; ⊗, K_4.

and

$$(2K_1P_{O_2})[Ch]^2 + (1 + K_2P_{O_2})[Ch] - [Ch]_0 = 0$$

where $[Ch]_0$ is initial gross molal chelate concentration calculated upon the basis of single molecules. For scheme II, the relation used is

$$F = P_{O_2}\frac{K_3 + 2K_3K_4P_{O_2}}{1 + K_3P_{O_2} + K_3K_4P_{O_2}^2}$$

It thus appears that if all the chelate molecules and their oxygen complexes contain chelate as Ch_2, the dimer, F is independent of initial chelate concentration, but if the molecules contain chelate as the single molecule, the gross chelate concentration becomes a factor in the value of F. The dependency of F upon concentration, given in Fig. 7, is compared with the dependency calculated for scheme I from the values of K_1 and K_2 derived above (Fig. 11). It is seen that whatever concentration dependency might be considered to exist outside experimental error falls between the absolute constancy predicted for scheme II and the trend calculated for scheme I. The values of K_1 and K_2 are such that the concentration dependency in this case is not very great for scheme I.

The values of K_1 and K_2 as dependent upon the 3-substituent in the chelate (Table III) do not seem to fall into significant order, perhaps because of a lack of a wider range of data.

TABLE III

SUBSTITUENT EFFECTS

Substituent	K_1	K_2
—OC_2H_5	2700	9.1
—F	1000	2.5
—NO_2	1200	1.3
—H	530	2.2

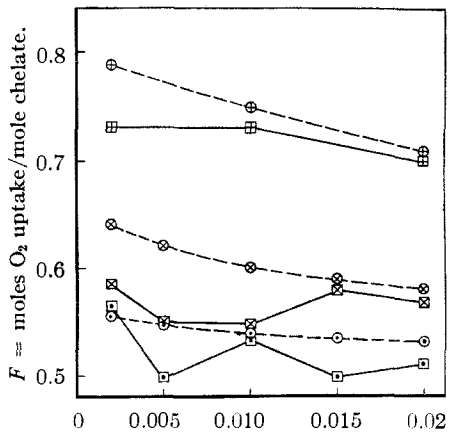


Fig. 11.—Concentration dependency of F for scheme I (K_1, K_2) compared with experiment:

P_{O_2} cm.	from K_1, K_2	Expt.
13	⊙	⊡
20	⊗	⊠
60.5	⊕	⊞

When the data for ethyl benzoate solutions and α-methylnaphthalene solutions were attacked according to scheme I, the following results were obtained: (ethyl benzoate) $K_1 = 15000$, $K_2 = 3.8$; (α-methylnaphthalene) $K_1 = 4600$, $K_2 = 14$. However, the curve for ethyl benzoate solutions is not accurately reproduced; only a smooth curve similar to those of Fig. 6 but falling close to the inflected curve of the actual data is obtained. No explanation, or proposed system of equilibria, is offered in explanation of the sigmoid curve, whose inflection seems real enough.

From simplicity, and from lack of substantial collateral reason for suspecting dimerization[6] in these chelates, we prefer reaction scheme I. It is of some interest that the ΔH values obtained for scheme I are not far from the calorimetrically determined value of 15 kcal./mole oxygen for the solid compounds of the same type. However, before any definite choice can be made, an independent experiment leading to the determination of extent of polymerization, if any, must be made.

Summary

The equilibrium for the reversible oxygenation of certain cobalt chelate molecules in solution in organic solvents has been measured. It has been shown that no simple single equilibrium can account for the observed result. Suggestions of possible reaction pairs are made.

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(6) Attempts to detect and determine dimerization by spectroscopic means failed to give entirely unequivocal results because of the impossibility of carrying the spectroscopic examination far enough into the blue in quinoline solution.