

## Optimum Conditions for Determination of the Stability of Weak Complexes

GUNNAR NORHEIM\*

*Chemical Institute A, University of Oslo, Blindern, Oslo 3, Norway*

The optimum conditions for the spectrophotometric determination of the stability constant of weak complexes have been calculated for various compositions and different values of the stability constant. The ratio between the initial concentrations of the reactants at the optimum conditions are found from tables given.

When determining the composition, the stability constant, and the extinction coefficient of a weak complex, it is of considerable importance to choose the optimum conditions of measurement. The initial concentration of the reactants should be within certain limits depending on the stability constant, the extinction coefficient, and the composition. In the present paper the optimum conditions have been calculated for various compositions and stability constants.

Hammond,<sup>1</sup> using the Benesi-Hildebrand plot,<sup>2</sup> discusses the optimum conditions for some special cases. Person<sup>3</sup> stated that the most accurate value for the stability constant of a complex is obtained when the equilibrium concentration of the complex is of the same order of magnitude as the equilibrium concentration of the more dilute component. If  $a$  is the initial concentration of the component in excess, and  $K$  is the stability constant, then according to Person,<sup>3</sup>  $0.1/K < a < 9.0/K$  for a 1:1 complex.

For weak complexes with other compositions it is more difficult to calculate the optimum conditions. In the present investigation the optimum conditions were calculated for a selection of complexes with different compositions, stability constants and extinction coefficient.

---

\* Present address: Institute of Forensic Medicine, University of Oslo, Rikshospitalet, Oslo 1, Norway.

## THEORY

Considering the equilibrium:



the stability constant is:

$$K = \frac{c}{(a-mc)^m (b-nc)^n} \quad (2)$$

where  $c$  is the concentration of complex, and  $a$  and  $b$  are the initial concentrations of A and B. This can be transformed into

$$(a-mc)^m (b-nc)^n - c/K = 0 \quad (3)$$

and if  $y=c/b$  and  $x=a/b$ , this becomes

$$(x-my)^m (1-ny)^n - y/Kb^{m+n-1} = 0 \quad (4)$$

$100 \times ny$  is the percentage of B complexed. If  $b$  is kept constant,  $a$  is varied, and  $1/Kb^{m+n-1}$  is chosen,<sup>4</sup>  $x$  and  $y$  can be calculated from eqn. (4). The coefficient  $1/Kb^{m+n-1}$  is defined by

$$W = 1/Kb^{m+n-1} \quad (5)$$

Presupposing the validity of the Beer-Lambert law, the extinction  $E = \epsilon dc$  where  $\epsilon$  is the molar extinction coefficient,  $d$  is the cell length and  $c$  the concentration of the complex. At infinite excess of A the above expression becomes  $E_0 = \epsilon db/n$ . Thus

$$W = \frac{(\epsilon d)^{m+n-1}}{K(nE_0)^{m+n-1}} \quad (6)$$

$W$  is not a constant for a given complex ( $nE_0$  and  $d$  can have different values), but the expression is useful for establishing the optimum conditions.  $W$  is particularly useful for calculating theoretical mole ratio curves.  $W$  determines the form of the mole ratio curve, and it is a measure of the deviation from the curve of the infinite stable complex this being only straight lines. Therefore  $W$  is the limiting factor when spectrophotometric data are used to determine the stability of complexes. It also demonstrates the importance of choosing the right cell length, especially for complexes where  $m$  or  $n$  are greater than 1.

## OPTIMUM CONDITIONS

It was considered of interest to calculate the optimum conditions in order to establish the value of  $y$  which gives the best value of  $K$ . If it is assumed that it is the standard deviation  $\sigma_y$  in  $y$  which mainly determines the standard deviation  $\sigma_K$  in  $K$ , it can be shown from eqn. (4) that

$$\sigma_K = \sqrt{\left(\frac{\partial K}{\partial y} \sigma_y\right)^2} = K \left(\frac{1}{y} + \frac{m^2}{x-my} + \frac{n^2}{1-ny}\right) \sigma_y \quad (7)$$

where  $y=c/b$  and  $x=a/b$ . A combination of eqns. (4) and (7) gives:

$$\frac{\sigma_K}{nK\sigma_y} = \frac{1}{ny} + \frac{m^2}{n} \left( \frac{(1-ny)^n Kb^{m+n-1}}{y} \right)^{1/m} + \frac{n}{1-ny} \quad (8)$$

Eqn. (8) can be expressed graphically with  $\sigma_K/nK\sigma_y$  as ordinate and  $ny$  as abscissa,  $ny$  being varied between 0 and 1.0. The function has one minimum in this range. For 1:1 complexes  $\sigma_K/K\sigma_y$  has its minimum value for  $y=y_{op}$

$$y_{op} = \frac{Kb+1}{Kb} \left( 1 - \frac{1}{\sqrt{Kb+1}} \right) \quad (9)$$

It can be shown that  $y_{op} > 0.5$  when  $Kb > 0$ .

In Fig. 1 curves are drawn for some special compositions and values of  $W$ . The equation for these curves can be written  $z=f(ny)$ , where  $z=\sigma_K/nK\sigma_y$ . From these curves  $z_{min}$  can be found, the abscissa in this point gives the optimum value of  $ny$ .

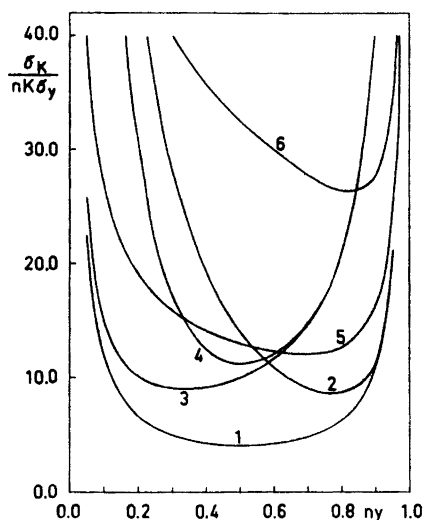


Fig. 1.  $\sigma_K/nK\sigma_y$  drawn as function of  $ny$ .  
Curve 1: 1:1  $W=10.0$ ; Curve 2: 1:1  $W=0.1$ ;  
Curve 3: 1:4  $W=10.0$ ; Curve 4: 1:4  $W=0.1$ ;  
Curve 5: 4:1  $W=10.0$ ; Curve 6: 4:1  $W=0.1$ .

For these curves the ordinate is a measure for the relative error in  $K$ , this error is smallest for the weakest complexes. For high values of  $W$  there is little difference in the ordinate values for the different compositions. For  $W=1.0$  and  $0.1$  the curves are more different, and this restricts the abscissa values that can be used. The curves for  $W > 10$  would have been similar to the  $W=10$  case.

When calculating the curves in Fig. 1, it was assumed that the standard deviation  $\sigma_x$  in the  $x$  is zero, but curves with the same ordinate can be calculated for any value of the ratio  $\sigma_x/\sigma_y$ . In practical cases one has always the fact that  $\sigma_x < \sigma_y$ , and for reasonable values of  $\sigma_x/\sigma_y$  the curves would be only slightly different from those in Fig. 1. For  $\sigma_x/\sigma_y=0.25$  the ordinate values increase with less than 2 %.

## OPTIMUM FACTOR

From eqn. (8) the minimum in the ordinate  $z_{\min}$  can be found. The abscissa value in this point is designated  $y_{\text{op}}$  and for this value  $x_{\text{op}}$  can be found from eqn. (4). When determining the stability constant of a weak complex,  $x=a/b$  should be varied around the value  $x=x_{\text{op}}$ .

To classify theoretical spectrophotometric data calculated from eqn. (4), an optimum factor  $N_{\text{op}}$  has been defined. For an ordinate  $z_1 > z_{\min}$  the line  $z=z_1$  is drawn (Fig. 1). The abscissa values in the points of intersection between this line and the curve  $z=f(ny)$  are designated  $ny_1$  and  $ny_2$ . The area limited by this line and the curve  $z=f(ny)$  is defined as the optimum factor  $N_{\text{op}}$

$$N_{\text{op}} = z_1(ny_2 - ny_1) - \int_{ny_1}^{ny_2} f(ny) d(ny) \quad (10)$$

When  $y_1$  and  $y_2$  are given, the corresponding values  $x_1$  and  $x_2$  can be found from eqn. (4).  $N_{\text{op}}$  is independent of  $z_{\min}$ , but the integral designated  $I_N$  is a measure of the ratio between the relative error in  $K$  and  $ny$ .

## CONCENTRATION RANGE

The concentrations at the optimum conditions, *i.e.*  $x=a/b$ , are calculated from eqn. (4) for different values of  $y$ . At an infinite excess of A,  $y_0=1/n$ .  $x_1$ ,  $x_2$  and  $x_{\text{op}}$  can be calculated for a given value of  $N_{\text{op}}$ , this giving the concentration range in which the mole ratio between A and B can be varied.  $y$  is proportional to the extinction:  $y=E/\epsilon db$ , corresponding to an extinction coefficient  $\epsilon=nE_0/db$ .

## CALCULATIONS

To calculate the optimum conditions a special computer program was made. With this program calculations can be made for any composition  $m:n$  and for any value of  $W$ . The results of some different cases are given in Table 1. The calculations have been made for  $N_{\text{op}}=1.0, 2.0$ , and  $3.0$ , for  $W=1.0 \times 10^4, 1.0 \times 10^3, 1.0 \times 10^2, 10.0, 1.0$  and  $0.1$  and for the following compositions: 1:1, 1:2, 1:3, 1:4, 2:2, 2:1, 3:1, and 4:1.

Table 1 gives  $ny_{\text{op}}$  and  $x_{\text{op}}$  for  $z=z_{\min}$ . For a given value  $N_{\text{op}}$ ,  $x_1$  and  $x_2$  corresponding to  $ny_1$  and  $ny_2$  are tabulated together with the integral  $I_N$ . Thus when determining the exact stability constant for a weak complex the optimum concentration range can be found from this table.

## APPLICATION

When the stability constant of a given complex is going to be determined, an initial value  $K_1$  for the stability constant is chosen. Then a suitable value for the concentration of the component kept constant must be found, this concentration should give suitable extinctions. A value for  $W$  is then selected

Table 1. Optimum conditions for different stabilities and compositions.

W	m:n	ny <sub>op</sub>	x <sub>op</sub>	N <sub>op</sub> =1.0					N <sub>op</sub> =2.0					N <sub>op</sub> =3.0				
				ny <sub>1</sub>	x <sub>1</sub>	ny <sub>2</sub>	x <sub>2</sub>	I <sub>N</sub>	ny <sub>1</sub>	x <sub>1</sub>	ny <sub>2</sub>	x <sub>2</sub>	I <sub>N</sub>	ny <sub>1</sub>	x <sub>1</sub>	ny <sub>2</sub>	x <sub>2</sub>	I <sub>N</sub>
10 <sup>4</sup>	1:1	0.50	10000	0.20	2500	0.80	40000	2.8	0.15	1800	0.85	56000	3.5	0.12	1400	0.88	70000	3.9
	1:2	0.41	6000	0.17	1200	0.71	44000	3.6	0.13	850	0.77	74000	4.5	0.11	680	0.81	107000	5.1
	1:3	0.37	4800	0.15	800	0.66	54000	4.2	0.12	560	0.72	107000	5.3	0.10	440	0.76	170000	6.0
	1:4	0.33	4200	0.14	610	0.61	69000	4.7	0.11	420	0.68	160000	5.9	0.09	330	0.72	280000	6.8
	2:2	0.42	78	0.17	35	0.71	210	3.6	0.13	29	0.77	270	4.5	0.11	26	0.81	330	5.1
	2:1	0.50	102	0.20	50	0.80	200	2.8	0.15	43	0.85	240	3.5	0.13	38	0.88	270	3.9
	3:1	0.52	24	0.21	14	0.81	37	3.0	0.16	13	0.85	41	3.7	0.13	11.8	0.88	44	4.2
	4:1	0.55	13	0.23	8.3	0.82	18	3.7	0.17	7.4	0.86	19	4.5	0.14	6.9	0.89	20	5.1
10 <sup>3</sup>	1:1	0.50	1000	0.20	250	0.80	4000	2.8	0.15	180	0.85	5600	3.5	0.12	140	0.88	7000	3.9
	1:2	0.41	600	0.17	120	0.71	4400	3.6	0.13	85	0.77	7400	4.5	0.11	68	0.81	10700	5.1
	1:3	0.37	480	0.15	80	0.66	5400	4.2	0.12	56	0.72	10700	5.3	0.10	44	0.76	17000	6.0
	1:4	0.33	420	0.14	61	0.61	6900	4.7	0.11	42	0.68	16000	5.9	0.09	33	0.72	28000	6.8
	2:2	0.42	25	0.17	11.3	0.72	67	3.6	0.13	9.5	0.77	87	4.5	0.11	8.4	0.81	105	5.1
	2:1	0.51	33	0.20	16	0.80	66	2.9	0.15	14	0.85	77	3.5	0.13	12	0.88	86	4.0
	3:1	0.54	12	0.22	7.2	0.82	19	3.3	0.17	6.3	0.86	21	4.1	0.14	5.8	0.88	22	4.6
	4:1	0.58	8.4	0.25	5.3	0.83	11.8	4.3	0.19	4.6	0.87	13	5.3	0.15	4.3	0.89	13	5.9
10 <sup>2</sup>	1:1	0.50	101	0.20	25	0.80	410	2.8	0.15	18	0.85	570	3.5	0.13	14	0.88	710	3.9
	1:2	0.42	61	0.17	12	0.71	440	3.6	0.13	8.6	0.77	740	4.5	0.11	6.9	0.81	1070	5.1
	1:3	0.37	48	0.15	8.2	0.66	540	4.2	0.12	5.7	0.72	1070	5.3	0.10	4.5	0.76	1700	6.0
	1:4	0.33	42	0.14	6.2	0.61	690	4.7	0.11	4.2	0.68	1600	5.9	0.09	3.3	0.72	2800	6.7
	2:2	0.43	8.5	0.18	3.8	0.72	22	3.6	0.14	3.2	0.78	28	4.5	0.11	2.8	0.81	34	5.2
	2:1	0.52	11.5	0.21	5.6	0.81	22	3.0	0.16	4.7	0.86	26	3.7	0.13	4.2	0.88	29	4.2
	3:1	0.57	6.8	0.25	3.9	0.83	10.4	3.8	0.19	3.4	0.87	11.3	4.7	0.15	3.1	0.89	12	5.3
	4:1	0.63	6.1	0.29	3.7	0.85	8.3	5.3	0.22	3.2	0.88	8.8	6.6	0.18	2.9	0.90	9.1	7.3

Table 1. Continued.

10	1:1	0.51	11.0	0.21	2.9	0.81	42	2.8	0.16	2.1	0.85	58	3.5	0.13	1.7	0.88	73	4.0
	1:2	0.42	6.6	0.18	1.4	0.72	45	3.5	0.14	0.99	0.77	76	4.4	0.12	0.79	0.81	109	5.0
	1:3	0.37	5.2	0.16	0.93	0.66	55	4.1	0.12	0.65	0.72	109	5.2	0.10	0.52	0.76	180	5.9
	1:4	0.34	4.5	0.14	0.70	0.61	70	4.7	0.11	0.49	0.68	160	5.9	0.10	0.38	0.72	280	6.7
	2:2	0.46	3.3	0.20	1.5	0.73	7.7	3.7	0.16	1.2	0.78	9.8	4.7	0.13	1.06	0.81	11.7	5.3
1.0	2:1	0.57	4.8	0.25	2.3	0.83	8.6	3.4	0.19	1.9	0.87	9.8	4.2	0.16	1.7	0.89	10.7	4.8
	3:1	0.63	4.5	0.30	2.5	0.85	6.4	4.8	0.23	2.1	0.89	6.9	5.9	0.19	1.9	0.90	7.2	6.6
	4:1	0.69	5.0	0.35	3.0	0.88	6.4	6.7	0.27	2.5	0.90	6.7	8.4	0.22	2.2	0.92	6.9	9.5
	1:1	0.59	2.0	0.29	0.69	0.83	5.8	3.0	0.23	0.52	0.87	7.6	3.8	0.19	0.43	0.89	9.2	4.4
	1:2	0.48	1.15	0.25	0.35	0.73	5.5	3.3	0.20	0.26	0.79	8.9	4.2	0.17	0.21	0.82	13	4.9
0.1	1:3	0.42	0.88	0.22	0.22	0.67	6.4	3.8	0.18	0.16	0.73	12	4.9	0.15	0.13	0.76	20	5.6
	1:4	0.38	0.74	0.19	0.16	0.62	7.9	4.3	0.16	0.119	0.69	18	5.5	0.14	0.097	0.72	31	6.3
	2:2	0.53	1.6	0.28	0.80	0.75	3.2	3.8	0.22	0.64	0.80	4.0	4.9	0.18	0.55	0.83	4.6	5.7
	2:1	0.66	2.7	0.34	1.4	0.86	4.2	4.3	0.27	0.13	0.89	4.7	5.4	0.22	0.98	0.91	5.0	6.1
	3:1	0.72	3.5	0.40	2.1	0.89	4.7	6.1	0.31	1.7	0.91	4.9	7.8	0.26	1.5	0.92	5.1	8.9
0.1	4:1	0.77	4.4	0.45	2.8	0.91	5.4	8.4	0.36	2.3	0.92	5.6	10.8	0.30	2.0	0.93	5.7	12.4
	1:1	0.77	1.10	0.54	0.65	0.90	1.8	3.6	0.48	0.57	0.92	2.1	4.8	0.43	0.51	0.94	2.4	5.6
	1:2	0.65	0.59	0.47	0.32	0.80	1.4	2.9	0.42	0.27	0.84	2.0	3.9	0.38	0.24	0.86	2.7	4.5
	1:3	0.56	0.42	0.40	0.20	0.73	1.5	3.2	0.36	0.16	0.78	2.6	4.3	0.33	0.15	0.81	3.9	5.0
	1:4	0.50	0.33	0.35	0.14	0.68	1.7	3.6	0.31	0.113	0.73	3.6	4.8	0.29	0.100	0.76	6.0	5.6
0.1	2:2	0.65	1.17	0.44	0.71	0.80	1.8	3.8	0.37	0.58	0.84	2.1	5.2	0.32	0.50	0.86	2.4	6.2
	2:1	0.78	2.2	0.51	1.4	0.91	2.8	5.5	0.43	1.14	0.93	3.0	7.2	0.38	1.01	0.94	3.1	8.4
	3:1	0.81	3.2	0.54	2.1	0.92	3.8	7.6	0.45	1.8	0.94	3.9	10.0	0.39	1.6	0.94	4.0	11.7
	4:1	0.83	4.2	0.57	2.9	0.93	4.8	10.0	0.48	2.5	0.94	4.9	13.2	0.42	2.2	0.95	5.0	15.6

and from Table 1 the optimum concentration range is found. The solutions are then prepared and the extinctions are measured, from these data a new  $K_2$  is calculated. By consulting Table 1 again, the concentrations can be corrected and a new optimum concentration range found. New solutions are prepared and measured. These measurements give a new stability constant  $K_3$ . This process must be repeated until the calculations give a stability constant  $K_n$  which corresponds to the optimum conditions chosen for this particular series of measurements.

## REFERENCES

1. Hammond, P. R. *J. Chem. Soc.* **1964** 479.
2. Benesi, H. A. and Hildebrand, J. H. *J. Am. Chem. Soc.* **71** (1949) 2703.
3. Person, W. B. *J. Am. Chem. Soc.* **87** (1965) 167.
4. Klausen, K. S. and Langmyhr, F. *J. Anal. Chim. Acta* **40** (1968) 167.

Received December 2, 1968.