TABLE IV
ABSORBANCIES AND $\bar{n}$ VALUES FOR 1-METHYL- AND 1-CYCOOHEXYLTETRAZOLE AND 0.001 *M* COBALT CHLORIDE HEXAHYDRATE IN TETRAHYDROFURAN

[L], *M*	−log [L]	A605 mμ	$\bar{n}$
	1-Methyltetrazole		
0.000		0.108	0.000
.003	2.52	.138	.316
.004	2.40	.145	.388
.005	2.30	.153	.469
.006	2.22	.159	.530
.007	2.15	.165	.592
.008	2.10	.171	.653
.009	2.05	.174	.683
.010	2.00	.180	.745
.030	1.52	.230	1.255
.050	1.30	.247	1.428
.500	0.30	.305	2.000
	1-Cyclohexyltetrazole		
0.000		0.108	0.000
.010	2.00	.185	.773
.012	1.92	.190	.829
.014	1.86	.198	.917
.016	1.80	.202	.961
.018	1.74	.209	1.028
.020	1.70	.209	1.028
.040	1.40	.238	1.359
.060	1.22	.265	1.657
.080	1.10	.278	1.801
.100	1.00	.290	1.934
.500	0.30	.318	2.000

TABLE V
FORMATION CONSTANTS FOR SOME COMPLEXES OF COBALT AND NICKEL WITH 1-SUBSTITUTED TETRAZOLES AT 25°; 90% CONFIDENCE LIMITS ARE GIVEN

Metal halide	Tetrazole	β_1	β_2	Solvent
$NiCl_2$	1-Methyl	3.8 ± 3.8	112 ± 10	Absolute ethanol
$NiCl_2$	1-Cyclohexyl	13.8 ± 4.0	112 ± 12	Absolute ethanol
$CoCl_2$	1-Methyl	135 ± 5	$3.3 \pm 0.1 \times 10^3$	Tetrahydrofuran
$CoCl_2$	1-Cyclohexyl	145 ± 25	$3.2 \pm 0.5 \times 10^3$	Tetrahydrofuran

Infrared spectra show no uniform shifts which can be associated with the coordination to the metals. The hydrochlorides, wherein bonding of the additional proton is probably at the 1-nitrogen, cause the "ring" vibrations[12] to shift to lower frequencies, while the shifts occur toward higher frequencies for the metal complexes, thus supporting the idea that there is a general metal–ring interaction.

At present it is difficult to speculate concerning the nature or site of the metal–tetrazole link. If tetrazoles were satisfying two coordination sites, then one might expect the solids would be ionic, $MT_2^{+2} + 2Cl^-$, and so have solubility in polar solvents. If tetrazole satisfied only one site, then a neutral species, MT_2Cl_2, would possibly result and greater solubility in nonpolar solvents would be expected. It seems likely the polymeric species may have formed.[2] In solution the species are probably simple monomeric ions or molecules, but upon crystallization polymeric species may form.

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CONTRIBUTION FROM THE COATES CHEMICAL LABORATORIES,
LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA

Studies on Some Metal Chelates of β-Furfuraldoxime[1a]

BY KANAN M. J. AL-KOMSER[1b,c] AND BUDDHADEV SEN[1d]

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Metal chelate formation by β-furfuraldoxime, a weak acid, was followed potentiometrically by observing the continuous change in hydrogen ion activity using Bjerrum's titration technique. The titrations were performed in a mixed solvent of 75% dioxane and 25% water by volume in an atmosphere of nitrogen. The step formation constants of metal β-furfuraldoximates at different ionic strengths and temperatures were computed through the determination of degree of formation of the system, $\bar{n}$, and measurement of unbound ligand concentration. The metals studied were chromium(III), iron(III), cobalt(III), nickel(II), copper(II), zinc, and lead. The order of magnitude of the stability constants and other indirect evidences indicated that the anion of β-furfuraldoxime exerted a strong ligand field. The values of the formation constants in mixed solvent were extrapolated to zero ionic strength, and these have been defined as the thermodynamic formation constants. The difference between this constant and aqueous standard constant has been explained. Standard entropy change for chelation in the case of iron(III) was a large negative quantity.

We have undertaken a comprehensive study of a number of chelates involving related ligands with a long-range view to correlate the thermodynamics of chelation, absorption spectra, magnetic properties, and thermal stability of these chelates with respect to solvent, properties of the central atom (ionization potential, d-orbital configuration, oxidation state), properties of donor atoms, and their steric orientation in a ligand molecule. This paper reports the thermodynamics of chelation by β-furfuraldoxime. Although it appears that of the various aspects of a chelate men-

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(1) (a) Presented before the Division of Inorganic Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963; (b) taken from Ph.D. dissertation of K. M. J. Al-Komser; (c) financial support provided by the Government of Iraq to K. M. J. Al-Komser during these studies is gratefully acknowledged; (d) requests for reprints should be directed to B. Sen.

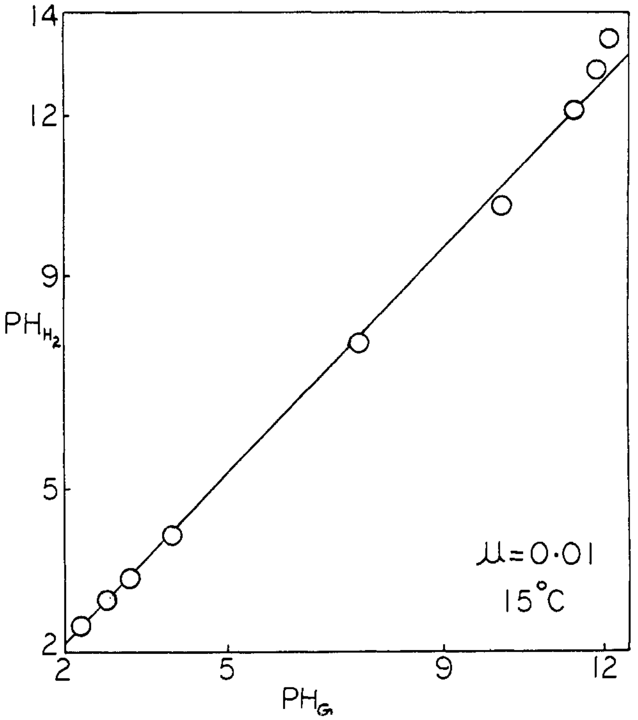

Fig. 1.—Calibration of glass electrode. A plot of nominal pH meter scale reading (pH_G) *vs.* corrected hydrogen electrode reading (pH_{H_2}).

tioned above, the study of the thermodynamics is the most promising one and simplest to approach, in reality such a study is beset with many difficulties. During the past two decades, numerous investigators have been engaged in determining stability constants under a variety of experimental conditions. The more meaningful among these values have been compiled by Bjerrum, *et al.*,[2a] in two volumes. However, most of these values are reliable concentration stability constants. In fact, the experimental difficulties and the uncertainties involved in determining thermodynamic stability constants are so numerous that these have led Rossotti and Rossotti[2b] to conclude that reliable stoichiometric constants are more useful than less certain values of the thermodynamic constants. In spite of this valid conclusion, it is a highly desirable endeavor to obtain thermodynamic constants even though these are only stabilities relative to the solvated species. It would be desirable to extrapolate the values of stability constants to zero ionic strength even when they are measured in mixed aqueous–organic solvents and consider these values as thermodynamic constants. The only fact to remember is that these values differ from standard thermodynamic constants by a factor which corresponds to the free energy change involved in transferring the reacting solutes from aqueous solution to mixed solvent, which has been termed by Owen[3,4] as the primary medium effect. Irving and Rossotti[5] have derived an explicit relation between the concentration equilibrium constant in water and the concentration equilibrium constant in mixed solvent. For the equilibrium M + Ke = MKe

$$\ln K_{(o)\mathrm{MKe}} - \ln K_{(w)\mathrm{MKe}} = \frac{1}{RT}[(\bar{G}^0{}_{(o)\mathrm{M}} - \bar{G}^0{}_{(w)\mathrm{M}}) + (\bar{G}^0{}_{(w)\mathrm{MKe}} - \bar{G}^0{}_{(o)\mathrm{MKe}} + (\bar{G}^0{}_{(o)\mathrm{Ke}} - \bar{G}^0{}_{(w)\mathrm{Ke}})] + \ln \frac{Y_{(o)\mathrm{M}} Y_{(w)\mathrm{MKe}} Y_{(o)\mathrm{Ke}}}{Y_{(o)\mathrm{MKe}} Y_{(w)\mathrm{M}} Y_{(w)\mathrm{Ke}}} \quad (1)$$

where $K_{(o)\mathrm{MKe}}$ is the concentration equilibrium constant in the mixed solvent; $K_{(w)\mathrm{MKe}}$ is the concentration equilibrium constant in water; $\bar{G}^0{}_{(o)s}$ is the partial molar free energy of the species s in mixed solvent; $\bar{G}^0{}_{(w)s}$ is the partial molar free energy of the species s in water; $Y_{(o)s}$ is the activity coefficient of the species s in mixed solvent, referred to unit activity coefficient at infinite dilution in water; and $Y_{(w)s}$ is the activity coefficient in water referred to unit activity coefficient at infinite dilution. By definition[3] the term within the bracket is the primary medium effect and the logarithmic term on the right-hand side is the secondary medium effect. If we now consider the equilibria in the mixed solvent and water, both at zero ionic strength, and rewrite eq. 1, remembering that

$Y_{(w)s} = 1$, at zero ionic strength

$$\ln K_{(o)\mathrm{MKe}} + \ln \frac{Y_{(o)\mathrm{MKe}}}{Y_{(o)\mathrm{M}} Y_{(o)\mathrm{Ke}}} - \ln K_{\mathrm{T}(w)\mathrm{MKe}} = 1/RT[(\bar{G}^0{}_{(o)\mathrm{M}} - \bar{G}^0{}_{(w)\mathrm{M}}) + (\bar{G}^0{}_{(w)\mathrm{MKe}} - \bar{G}^0{}_{(o)\mathrm{MKe}}) + (\bar{G}^0{}_{(o)\mathrm{Ke}} - \bar{G}^0{}_{(w)\mathrm{Ke}})] \quad (2)$$

where K_{T} refers to the thermodynamic constant. Combination of the first two terms on the left-hand side is also a true thermodynamic constant, thus

$$\ln K_{\mathrm{T}(o)\mathrm{MKe}} - \ln K_{\mathrm{T}(w)\mathrm{MKe}} = 1/RT[(\bar{G}^0{}_{(o)\mathrm{M}} - \bar{G}^0{}_{(w)\mathrm{M}}) + (\bar{G}^0{}_{(w)\mathrm{MKe}} - \bar{G}^0{}_{(o)\mathrm{MKe}}) + (\bar{G}^0{}_{(o)\mathrm{Ke}} - \bar{G}^0{}_{(w)\mathrm{Ke}})] \quad (3)$$

where $K_{\mathrm{T}(o)\mathrm{MKe}}$ and $K_{\mathrm{T}(w)\mathrm{MKe}}$ are the thermodynamic formation constants of the species MKe in the mixed solvent and water, respectively. These two thermodynamic constants differ from each other by $1/RT$ times the algebraic sum of the free energy of transfer of the reactants and the product from one solvent to the other. The important assumptions implicit in the foregoing derivation are (i) there is no other interaction in either medium besides the explicit equilibrium and solvation and (ii) the secondary medium effect term, the second term on the left-hand side of eq. 2, corrects for the deviation due to ion association in organic or low dielectric constant medium. Thus, we see that the extrapolation of equilibrium measurement in mixed solvent to zero ionic strength is not only justifiable and desirable, but very meaningful. In fact, it is our opinion that this method will possibly yield more realistic data compared to those which may be obtained through the use of the extended Debye–Hückel equation and arbitrary values of ion size parameter.

The formation constants of metal β-furfuraldoximates reported in this paper were measured in 75% by volume dioxane and 25% by volume water. Computation of

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(2) (a) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Parts I and II, The Chemical Society, London, 1957, 1958; (b) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Company, Inc., New York, N. Y., 1961.

(3) B. B. Owen, *J. Am. Chem. Soc.*, **54**, 1758 (1932).

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950.

(5) H. Irving and H. Rossotti, *Acta Chem. Scand.*, **10**, 72 (1956).

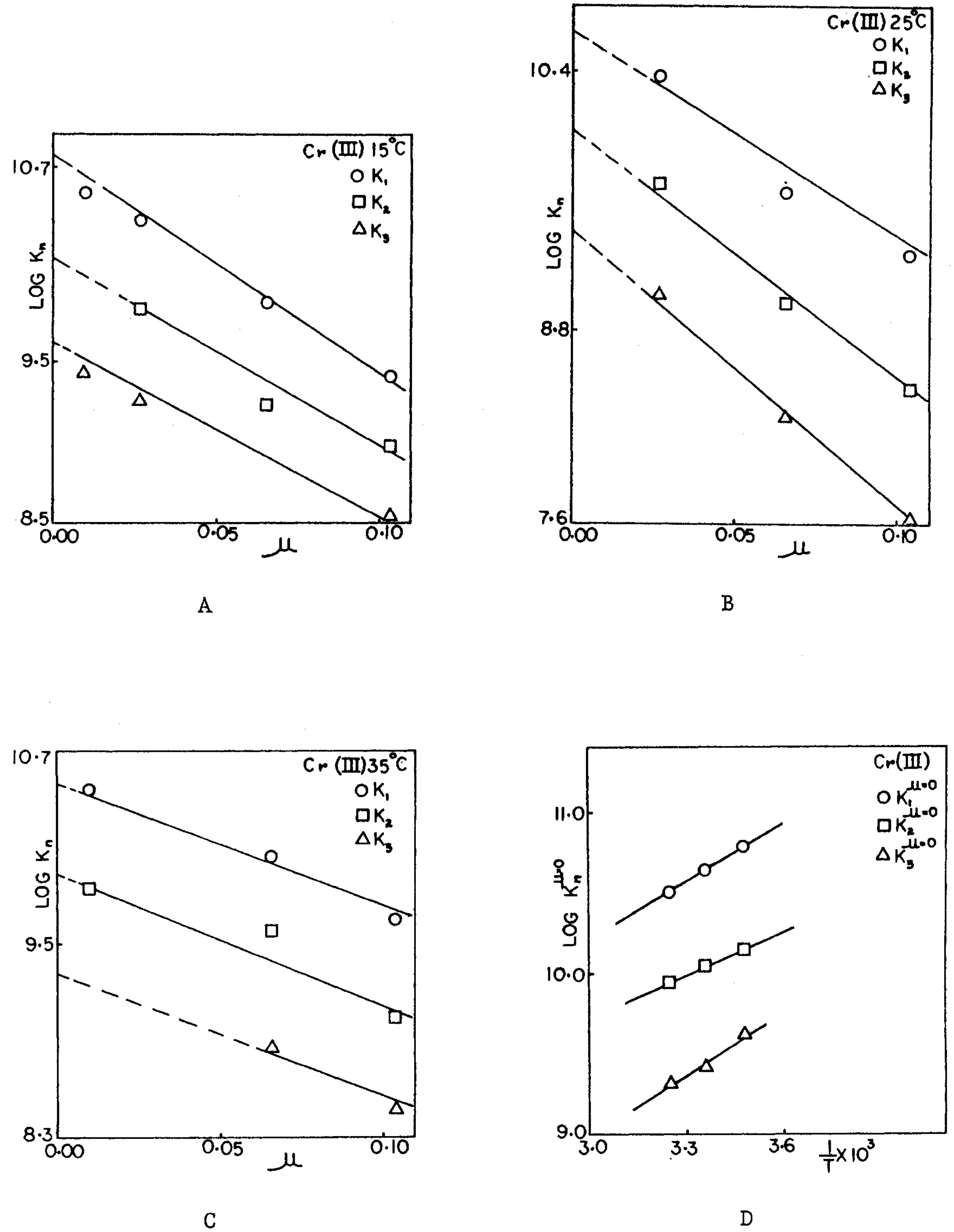

Fig. 2.—A, B, C: Plots of step concentration formation constants of chromium(III)–β-furfuraldoxime against ionic strength at different temperatures (A, 15°; B, 25°; and C, 35°). D: Plots of step thermodynamic formation constants of chromium(III)–β-furfuraldoxime against reciprocal of absolute temperature.

formation constants was done by Bjerrum's method,[6] which has been discussed exhaustively in a recent review by Sen.[7] The values of the formation constants were obtained from the experimental data both by graphical and mid-point slope methods.[7]

Experimental

All metal salt solutions excepting iron(II) were prepared from reagent grade nitrates. Iron(II) perchlorate solution was prepared by dissolving a calculated amount of electrolytic iron powder in a calculated amount of perchloric acid. Metal solutions were standardized by conventional procedures. All solutions were 0.05 *M* with respect to the metal ion and 0.0074 *M* with respect to nitric or perchloric acid. The inert salt solution used to adjust the ionic strength was 1.0 *M* sodium perchlorate. β-Furfuraldoxime (m.p. 91–92°) was obtained from Eastman Kodak Co. and was used as such. *p*-Dioxane was obtained from Eastman Kodak Co. and was purified,[8] stored, and dispensed under an atmosphere of nitrogen.

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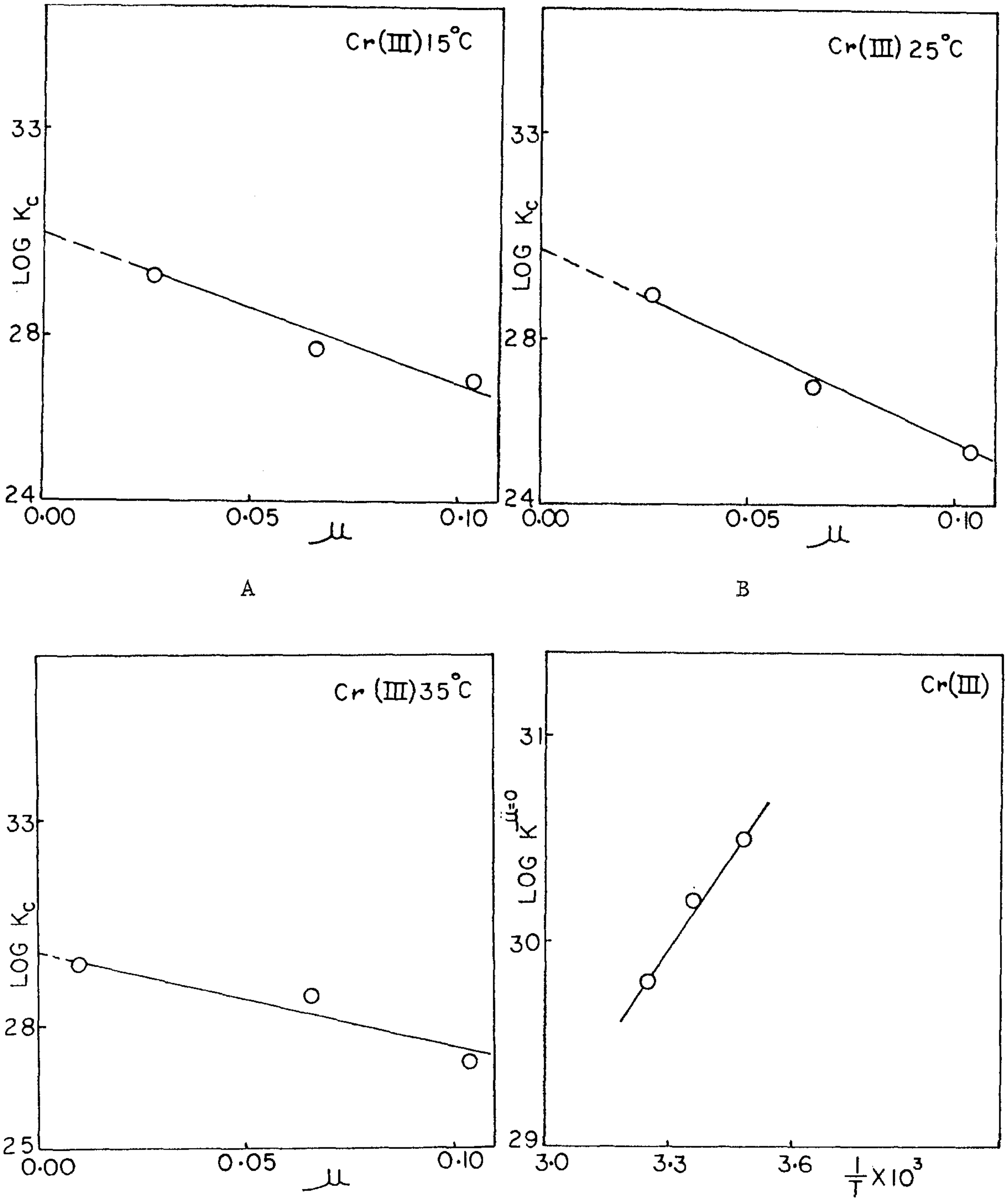
[6] J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Sons, Copenhagen, 1941.

[7] B. Sen, *Anal. Chim. Acta*, **27**, 515 (1962).

[8] M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).



A

B

C

D

Fig. 3.—A, B, C: Plots of over-all concentration formation constants (K_c) of chromium(III)–β-furfuraldoxime against ionic strength at different temperatures (A, 15°; B, 25°; and C, 35°). D: Plot of over-all thermodynamic formation constant of chromium(III)–β-furfuraldoxime against reciprocal of absolute temperature.

The titration technique used was similar to that used by Calvin and Wilson.[8] A Beckman Model G pH meter equipped with a saturated calomel electrode (s.c.e.) and a Beckman glass electrode (No. 40498, formerly 1190-80) was used to follow the titrations. The titration cell was a double walled glass vessel; water from the thermostat could be circulated through the annular space to maintain constant temperature. The cell was designed to accommodate the hydrogen electrode used for calibration of glass electrodes in the mixed solvent. The hydrogen electrode was designed according to Hills and Ives.[9] However, instead of using a bright platinum electrode and platinum black suspension, a very lightly platinized electrode in combination with platinum black suspension was used. This greatly shortened the time required for equilibration, which was only 10 to 15 min. instead of several hours. The solutions were stirred with a magnetic stirrer and titrations were carried out under an atmosphere of nitrogen.

Because the present studies were carried out in a mixed solvent system, it was necessary to calibrate the glass electrode. From a consideration of the following cells

I glass $|H^+, H_2O||KCl$ (satd. aq.) $|Hg_2Cl_2–Hg$
II glass $|H^+, H_2O$, org. $||KCl$ (satd. aq.) $|Hg_2Cl_2–Hg$
III Pt,H_2(1 atm.) $|H^+, H_2O$, org. $||KCl$ (satd. aq.) $|Hg_2Cl_2–Hg$

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[9] G. H. Hills and D. J. G. Ives, J. Chem. Soc., 305 (1951).

TABLE I

VALUES OF VAPOR PRESSURES, PARTIAL PRESSURES, MOLE FRACTIONS OF DIOXANE AND WATER IN 75% BY VOLUME DIOXANE AND 25% BY VOLUME WATER MIXTURES

Temp., °C.	P_D^{0a}	P_W^{0b}	N_D	N_W	P_D	P_W
15	23.50	12.80	0.371	0.629	8.72	8.05
25	40.00	23.80	.385	.615	15.40	14.65
35	64.00	42.20	.386	.614	24.70	25.85

[a] P_D^0 = vapor pressure of pure dioxane. [b] P_W^0 = vapor pressure of pure water. Other symbols have been explained in the text.

TABLE II

VALUES OF THE IONIZATION CONSTANTS OF β-FURFURALDOXIME AT VARIOUS TEMPERATURES AND IONIC STRENGTHS

Ionic strength, μ	Ionization constant, K_a
At 15°	
0.010	3.981×10^{-14}
.027	5.624×10^{-14}
.066	8.912×10^{-14}
.096	1.122×10^{-13}
.104	2.818×10^{-13}
At 25°	
.010	3.162×10^{-14}?
.027	2.512×10^{-13}
.066	3.548×10^{-13}
.096	5.624×10^{-13}
.104	7.943×10^{-13}
At 35°	
.010	3.162×10^{-13}
.027	5.012×10^{-13}
.066	6.310×10^{-13}
.096	1.259×10^{-12}
.104	1.585×10^{-12}

and assumption of unit activity coefficient, unit fugacity at low concentration and pressure of 1 atm., and ignoring secondary medium effects at low concentrations, it is possible to show that

$$\mathrm{pH_{gm}} - \mathrm{pH} = \mathrm{pH_{gw}} + \frac{F}{2.303RT}(E_{gm} - E_{gw} + E_j^w - E_{Pt/H_2(m)} + E_{s.c.e.}) \quad (4)$$

where $\mathrm{pH_{gm}}$ is the pH calculated from glass electrode measurement in mixed solvent with cell II; pH is the log a_{H^+}, calculated from e.m.f. measurement with cell III; $\mathrm{pH_{gw}}$ is the pH calculated from glass electrode measurement with cell I; E_{gm} is the e.m.f. of the glass electrode *vs.* s.c.e. in mixed solvent; E_{gw} is the e.m.f. of the glass electrode *vs.* s.c.e. in water; $E_{Pt/H_2(m)}$ is the e.m.f. of the hydrogen electrode *vs.* s.c.e. in the mixed solvent; E_j^w is the liquid junction potential at the interface in cell I; and $E_{s.c.e.}$ is the potential of the s.c.e. All the cells contained the same number of moles of hydrogen ion. It is seen that relation 4 does not contain any potential term due to the interface of aqueous solution and solution in the mixed solvent; in fact, such a term has dropped out. An implication of this is that the necessity of any correction for liquid junction potential due to the aqueous–mixed solvent interface is eliminated by the experimental set-up.

The pressure of hydrogen was corrected for the barometric pressure, partial pressures of water and dioxane in the mixed solvent, and the depth of the hydrogen jet during titration. Vapor pressures of pure dioxane, P_D^0, at various temperatures were read from Jordan's graph[10] and those for water were obtained from Bates.[11] Densities of 75% by volume dioxane–water mixture at various temperatures were obtained by interpolation and extrapolation of the data of Herz and Lorentz.[12] From these and knowing the density of pure dioxane and water, the partial pressures P_D and P_W of dioxane and water and their mole fractions N_D and N_W were calculated at different temperatures assuming that Raoult's law was obeyed (Table I). The corrected hydrogen pressure was then obtained by subtracting the partial pressures from the barometric pressure. The observed e.m.f. was then corrected for the pressure of hydrogen, and the correct pH in mixed solvent was calculated. The corrections were carried out at different temperatures and ionic strengths. Figure 1 shows a plot of the nominal pH meter scale reading ($\mathrm{pH_G}$) *vs.* the corrected pH ($\mathrm{pH_{H_2}}$) at 15° and ionic strength 0.01.

Chromium(III) reactions are well known for their sluggishness. Therefore, during the preliminary titrations, titrant was added at intervals of 60 min. Eventually it was found that constant e.m.f. is attained within 0.5 hr.

The ionization constant of β-furfuraldoxime, a very weak acid, was determined by measuring the pH on the half-neutralized reagent and correcting the measured pH from the calibration curves described earlier. Quite obviously the effect of hydrolysis was ignored. The reason for doing this was that the sophistication of calculation was deemed not justified by the refinement of the values, especially in this range. Table II summarizes the results.

TABLE III

COMPUTATION OF THE VALUES pKe AND DEGREE OF FORMATION, $\bar{n}$, FOR NICKEL(II) AT 35° AND μ = 0.01[a]

$\mathrm{pH_G}$[b]	$\mathrm{pH_{H_2}}$[c]	C_{H^+},[d] moles/l.	Total HKe,[e] mmoles	ΔV,[f] ml.	Bound $K\bar{e}$,[g] mmoles	Unbound HKe,[h] mmoles	V_f,[i] ml.	Unbound C_{HKe},[j] moles/l.	Unbound $C_{K\bar{e}}$,[k] moles/l.	pKe	$\bar{n}$
6.50	6.65	2.239×10^{-7}	2.5	0.10	0.50×10^{-2}	2.495	30.95	8.07×10^{-2}	11.4×10^{-8}	6.943	0.059
6.60	6.78	1.659×10^{-7}	2.5	.20	1.00×10^{-2}	2.490	31.05	8.01×10^{-2}	15.3×10^{-8}	6.815	.119
6.70	6.88	1.318×10^{-7}	2.5	.36	1.80×10^{-2}	2.482	31.20	7.96×10^{-2}	19.1×10^{-8}	6.719	.214
6.80	6.98	1.047×10^{-7}	2.5	.55	2.75×10^{-2}	2.472	31.40	7.88×10^{-2}	23.8×10^{-8}	6.623	.328
6.85	7.05	8.912×10^{-8}	2.5	.75	3.75×10^{-2}	2.462	31.70	7.78×10^{-2}	2.76×10^{-7}	6.559	.447
6.90	7.10	7.943×10^{-8}	2.5	1.24	6.20×10^{-2}	2.438	32.30	7.55×10^{-2}	2.01×10^{-7}	6.521	.738
6.95	7.15	7.080×10^{-8}	2.5	1.75	8.75×10^{-2}	2.412	32.60	7.40×10^{-2}	3.30×10^{-7}	6.482	1.040
7.00	7.20	6.310×10^{-8}	2.5	1.95	9.75×10^{-2}	2.402	32.85	7.31×10^{-2}	3.66×10^{-7}	6.437	1.160
7.10	7.30	5.012×10^{-8}	2.5	2.34	11.7×10^{-2}	2.383	33.25	7.17×10^{-2}	4.52×10^{-7}	6.345	1.395
7.20	7.40	3.981×10^{-8}	2.5	2.68	13.4×10^{-2}	2.366	33.55	6.06×10^{-2}	5.61×10^{-7}	6.251	1.595

[a] $M^{+2} = 1.68 \times 0.05 = 8.4 \times 10^{-2}$ mmole of total Ni(II) taken; total HKe taken = 2.5 mmoles; total volume before titration = 30 ml. [b] $\mathrm{pH_G}$ = nominal pH = pH meter reading, which is obtained from the titration curves. [c] $\mathrm{pH_{H_2}}$ = the value of $\mathrm{pH_G}$ on the hydrogen scale. [d] C_{H^+} = −antilog of $\mathrm{pH_{H_2}}$. [e] Total HKe = the total amount of HKe taken. [f] V = the horizontal distance in ml. of 0.05 M sodium hydroxide solution, between the titration curves without metal ion and with metal ion at a particular pH. [g] Bound $K\bar{e}$ = the number of millimoles of sodium hydroxide that corresponds to V. [h] Unbound HKe = total HKe − bound $K\bar{e}$. [i] V_f = final volume after each increment of sodium hydroxide. [j] C_{HKe} = molar concentration of unbound HKe = unbound HKe/V_f. [k] $C_{K\bar{e}}$ = molar concentration of unbound ligand, $K\bar{e}$, = K_aC_{HKe}/C_{H^+}, where K_a = ionization constant of HKe, HKe = β-furfuraldoxime.

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(10) T. E. Jordan, "Vapor Pressure of Organic Compounds," International Publishers, New York, N. Y., 1954.

(11) R. G. Bates, "Electrometric pH Determination," John Wiley and Sons, Inc., New York, N. Y., 1954.

(12) W. Herz and E. Lorentz, *Z. Physik. Chem.*, **A140**, 406 (1929).

TABLE IV

VALUES OF CONCENTRATION STABILITY CONSTANTS OF METAL β-FURFURALDOXIMATES AT DIFFERENT TEMPERATURES AND VARIOUS IONIC STRENGTHS

μ	log K_n	Cr(III)	Fe(III)[a]	Co(III)[a]	Ni(II)	Cu(II)	Zn(II)	Pb(II)
At 15°								
0.01	log K_1	10.54	12.75	...	6.39	10.09	...	...
	log K_2	9.73	11.58	...	5.99	9.57	...	...
	log K_3	9.43	10.41	...	...	...	...	...
	log K_c	29.19	34.74	...	12.38	19.66	...	...
0.027	log K_1	10.37	12.19	...	7.26	10.00	...	...
	log K_2	9.82	9.69	...	6.67	9.67	...	...
	log K_3	9.26	7.20	...	...	...	...	...
	log K_c	29.45	29.07	...	14.10	19.68	...	...
0.066	log K_1	9.86	10.90	8.00	6.83	9.42	...	...
	log K_2	9.23	9.02	...	6.19	9.19	...	...
	log K_3	8.60	7.12	...	...	...	...	...
	log K_c	27.69	27.06	...	13.24	18.62	...	...
0.096	log K_1	...	11.10	6.94	6.63	9.03	7.08	8.78
	log K_2	...	10.40	...	6.23	8.59	6.46	7.51
	log K_3	...	9.70	...	...	...	...	...
	log K_c	...	31.20	...	12.82	17.66	13.20	16.06
0.104	log K_1	9.41	10.91	7.33	6.76	8.99	6.79	7.53
	log K_2	8.98	8.89	...	6.30	...	6.38	7.88
	log K_3	8.55	6.88	...	...	...	...	...
	log K_c	26.94	26.67	...	13.00	...	13.58	15.41
At 25°								
0.01	log K_1	10.96	12.06	...	7.97	10.34	...	...
	log K_2	10.23	10.10	...	7.45	9.94	...	...
	log K_3	9.51	8.14	...	...	...	...	...
	log K_c	30.69	30.30	...	15.42	20.28	...	...
0.027	log K_1	10.37	11.25	...	7.24	9.81	...	...
	log K_2	9.70	9.30	...	7.01	9.48	...	...
	log K_3	9.02	7.36	...	...	...	...	...
	log K_c	29.09	27.90	...	14.28	19.28	...	...
0.066	log K_1	9.65	9.89	...	6.75	9.20	...	...
	log K_2	8.96	8.87	...	6.41	8.81	...	...
	log K_3	8.26	7.85	...	...	...	...	...
	log K_c	26.87	26.61	...	13.14	18.02	...	...
0.096	log K_1	...	11.37	7.79	6.87	8.47	6.46	8.55
	log K_2	...	9.34	7.00	5.76	8.14	5.96	7.33
	log K_3	...	7.31	5.60	...	...	...	...
	log K_c	...	28.02	20.09	12.00	16.50	12.20	15.70
0.104	log K_1	9.26	9.64	7.32	6.02	8.35	6.71	7.97
	log K_2	8.43	8.48	...	5.54	...	6.02	7.96
	log K_3	7.61	7.32	...	...	...	...	...
	log K_c	25.30	25.44	...	11.56	...	12.28	13.93
At 35°								
0.01	log K_1	10.46	12.83	...	6.56	9.64	...	...
	log K_2	9.84	9.51	...	6.30	9.24	...	...
	log K_3	8.80	6.19	...	...	...	...	...
	log K_c	29.51	28.53	...	12.98	18.88	...	...
0.027	log K_1	9.94	8.91	...	6.40	9.15	...	...
	log K_2	9.31	8.88	...	5.52	8.97	...	...
	log K_3	8.35	8.84	...	...	...	...	...
	log K_c	27.93	26.63	...	12.38	18.12	...	...
0.066	log K_1	10.04	6.67	...	7.05	9.27	...	...
	log K_2	9.58	9.22	...	6.40	8.98	...	...
	log K_3	8.86	11.76	...	...	...	...	...
	log K_c	28.73	27.65	...	13.76	18.26	...	...
0.096	log K_1	...	10.82	7.11	5.77	8.18	6.13	7.65
	log K_2	...	8.57	6.49	5.37	7.83	6.02	6.59
	log K_3	...	6.32	5.87	...	...	...	...
	log K_c	...	25.71	19.47	11.12	16.02	12.16	14.04
0.104	log K_1	9.65	9.03	7.62	6.57	8.71	6.74	6.59
	log K_2	9.04	8.83	...	6.14	...	...	...
	log K_3	8.47	8.62	...	...	...	...	...
	log K_c	27.12	26.48	...	12.70	...	...	...

[a] Although the starting materials were Fe(II) and Co(II), these were rapidly oxidized during titration. See Discussion. $K_c = K_{\text{over-all}}$.

Titration Curves.—It has already been mentioned that the titration technique used was similar to that used by Calvin and Wilson.[8] Two different solutions were titrated with standard sodium hydroxide solution in mixed solvent (75% dioxane–25% water by volume). The two solutions were identical except that one contained a metal ion and the other did not. The course of pH change during the titration was followed by a calibrated glass electrode. The difference in the amount of sodium hydroxide consumed in the two titrations is a measure of the extent of chelation. The shapes of these curves are now too familiar to chemists to justify their reproduction here. In order to construct the formation curve ($\bar{n}$ *vs.* pKe plot), it was required to calculate the quantity $\bar{n}$, defined by

$$\bar{n} = \frac{\sum_{1}^{N} nC_{\mathrm{MKe}_n}}{C_{\mathrm{M}} + \sum_{1}^{N} C_{\mathrm{MKe}_n}} \qquad (5)$$

and the concentration C_{Ke} of unbound ligand. The details of these calculations for only one case are given in Table III.

The formation curves were either (i) inverted S-shaped or (ii) almost a straight line, obviously with a negative slope, or (iii) a slightly upward concave curve again with negative slope. The stability constants were either read off directly from these curves or were calculated by the mid-point slope method.[7] The results are summarized in Table IV.

In the present investigation, the thermodynamic formation constants, as defined earlier, at different temperatures were obtained by extrapolation of measured formation constants to zero ionic strength in mixed solvent. Ligational standard free energy was obtained from $\Delta F° = -2.303RT \log K^{\mu = 0}$ and $K^{\mu = 0}$ = value of formation constant at zero ionic strength obtained by extrapolation.

The standard enthalpy of chelation was obtained from the free energy change at different temperatures using the relation

$$\Delta H° = 2.303R \left[\frac{T_1T_2}{T_2 - T_1} \log \frac{K_2}{K}\right]$$

where $T_2 > T_1$, and K_2 corresponds to T_2 and K_1 corresponds to T_1. When log K is plotted against $1/T$, the entire quantity within the bracket is given by the slope of the plot, from which $\Delta H°$ is easily calculated.

In the present work the data were treated in the following way. The values of log step formation constants at various ionic strengths at each temperature were extrapolated to zero ionic strength to give step thermodynamic formation. These values have been symbolized in Table V as log $K_1^{\mu = 0}$, log $K_2^{\mu = 0}$, and log $K_3^{\mu = 0}$. Their sum has been symbolized as calculated log $K^{\mu = 0}$. The values of over-all concentration formation constant K_{c}, at various ionic strengths, were likewise extrapolated to zero ionic strength at each temperature. The over-all thermodynamic formation constants thus obtained have been symbolized as experimental log $K^{\mu = 0}$. The values of log $K_n^{\mu = 0}$ and log $K^{\mu = 0}$ were then plotted against the reciprocal of absolute temperature to yield the values of step and over-all ligational enthalpies. Figures 2 and 3 show how the data were treated in the case of chromium(III). The log K_n *vs.* μ plots were always linear except in the case of iron(III) where they were concave upward. The log $K_n^{\mu = 0}$ *vs.* $1/T$ and log $K^{\mu = 0}$ *vs.* $1/T$ plots were always linear.

The ligational entropy was calculated from the relation

$$\Delta S° = \frac{\Delta H° - \Delta F°}{T}$$

The values of ligational free energies, entropies, and enthalpies are summarized in Tables V and VI.

TABLE V

THERMODYNAMIC VALUES OF METAL β-FURFURALDOXIMATES AT DIFFERENT TEMPERATURES

	Cr(III)	Fe(III)	Ni(II)	Cu(II)
		At 15°		
log $K_1^{\mu = 0}$	10.78	13.26	7.70	10.39
log $K_2^{\mu = 0}$	10.14	12.52	7.00	10.18
log $K_3^{\mu = 0}$	9.62	11.60	...	...
Calcd. log $K^{\mu = 0}$[a]	30.54	37.38	14.70	20.57
Exptl. log $K^{\mu = 0}$[b]	30.50	37.40	14.70	20.66
$\Delta F_1°$, kcal./mole	−14.21	−17.48	−10.15	−13.69
$\Delta F_2°$	−13.36	−16.50	−9.23	−13.42
$\Delta F_3°$	−12.68	−15.29	...	...
Calcd. $\Delta F°$	−40.25	−49.27	−19.38	−27.11
Exptl. $\Delta F°$	−40.20	−49.29	−19.38	−27.23
$\Delta S_1°$, e.u.	30.76	−18.75	−35.45	13.30
$\Delta S_2°$	32.26	High neg.	−6.08	−1.94
$\Delta S_3°$	23.85	High neg.	...	...
Calcd. $\Delta S°$	86.87	High neg.	−41.53	...
Exptl. $\Delta S°$	90.49	High neg.	−40.76	2.71
		At 25°		
log $K_1^{\mu = 0}$	10.64	12.64	7.60	10.28
log $K_2^{\mu = 0}$	10.04	10.80	7.52	9.88
log $K_3^{\mu = 0}$	9.42	8.52	...	...
Calcd. log $K^{\mu = 0}$	30.10	31.96	15.12	20.16
Exptl. log $K^{\mu = 0}$	30.20	32.05	15.08	20.54
$\Delta F_1°$, kcal./mole	−14.51	−17.24	−10.36	−14.02
$\Delta F_2°$	−13.69	−14.73	−10.26	−13.47
$\Delta F_3°$	−12.85	−11.62	...	...
Calcd. $\Delta F°$	−41.05	−43.59	−20.62	−27.49
Exptl. $\Delta F°$	−41.19	−43.72	−20.57	−28.01
$\Delta S_1°$, e.u.	30.74	−18.93	−33.56	13.96
$\Delta S_2°$	32.28	High neg.	−2.42	−1.71
$\Delta S_3°$	23.62	High neg.	...	...
Calcd. $\Delta S°$	86.64	High neg.	−35.98	...
Exptl. $\Delta S°$	90.77	High neg.	−35.40	5.24
		At 35°		
log $K_1^{\mu = 0}$	10.50	...	6.66	9.90
log $K_2^{\mu = 0}$	9.94	9.94	6.40	9.45
log $K_3^{\mu = 0}$	9.32	...	...	...
Calcd. log $K^{\mu = 0}$	29.76	...	13.06	19.35
Exptl. log $K^{\mu = 0}$	29.80	29.50	13.14	19.34
$\Delta F_1°$, kcal./mole	−14.80	...	−9.38	−13.95
$\Delta F_2°$	−14.01	−14.01	−9.02	−13.32
$\Delta F_3°$	−13.14	...	...	...
Calcd. $\Delta F°$	−41.95	...	−18.40	−27.27
Exptl. $\Delta F°$	−41.99	−41.57	−18.51	−27.26
$\Delta S_1°$, e.u.	30.68	...	−35.65	13.28
$\Delta S_2°$	32.27	High neg.	−6.36	−2.14
$\Delta S_3°$	23.80	...	...	...
Calcd. $\Delta S°$	86.75	...	−42.01	...
Exptl. $\Delta S°$	90.42	High neg.	−40.94	2.63

[a] Calcd. log $K^{\mu = 0}$ = log $K_1^{\mu = 0}$ + log $K_2^{\mu = 0}$ + log $K_3^{\mu = 0}$.
[b] Obtained by extrapolation of measured K_{c} to zero ionic strength.

TABLE VI

VALUES OF STANDARD ENTHALPY CHANGE FOR METAL β-FURFURALDOXIMATES

	Cr(III)	Fe(III)	Ni(II)	Cu(II)
$\Delta H_1°$, kcal./mole	−5.35	−22.88	−20.36	−9.86
$\Delta H_2°$	−4.07	−51.70	−10.98	−13.98
$\Delta H_3°$	−5.81	−114.30	...	...
Calcd. $\Delta H°$	−15.23	−188.88	−31.34	−23.84
Exptl. $\Delta H°$	−14.14	−152.33	−31.12	−26.45

Results and Discussion

Bryson and Dwyer[13] studied a number of metal β-furfuraldoximates and found the behavior of β-furfuraldoxime quite peculiar as a chelate former. These authors assigned the following structure to bis-β-furfuraldoxime palladium(II) and nickel(II)

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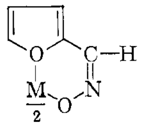
(13) A. Bryson and F. P. Dwyer, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 455 (1940).



According to these authors the product immediately formed on mixing the oxime and the metal ion in aqueous medium was not the above bis compound, but bis-(furfuraldoxime)-palladium(II) chloride, $Pd(C_5H_4O\cdot NOH)_2\cdot Cl_2$, in the case of palladium(II), and tris-(furfuraldoxime)-nickel(II), $Ni(C_5H_4O\cdot ON)_2\cdot C_5H_4O\cdot NOH$, but both these compounds rapidly changed to the bis compounds at alkaline pH in organic solvent. An identical condition prevailed during the present titration. Therefore, it is logical to assume that complex formed in the solution during the titration was the bis compound of nickel(II), copper(II), zinc, and lead(II) of the above structure. The shape of the titration and formation curves also confirmed this assumption. In the case of iron and cobalt, tris iron(III) and tris cobalt(III) compounds were formed although the metals were initially in the bivalent state. Bryson and Dwyer[13] also found the tris cobalt(III) compound to be very stable. In view of the reaction environment and the nature of the ligand, such oxidation of these metals will be rapidly brought about by traces of oxygen. The order of stability also suggested iron(III) and cobalt(III) complexes.

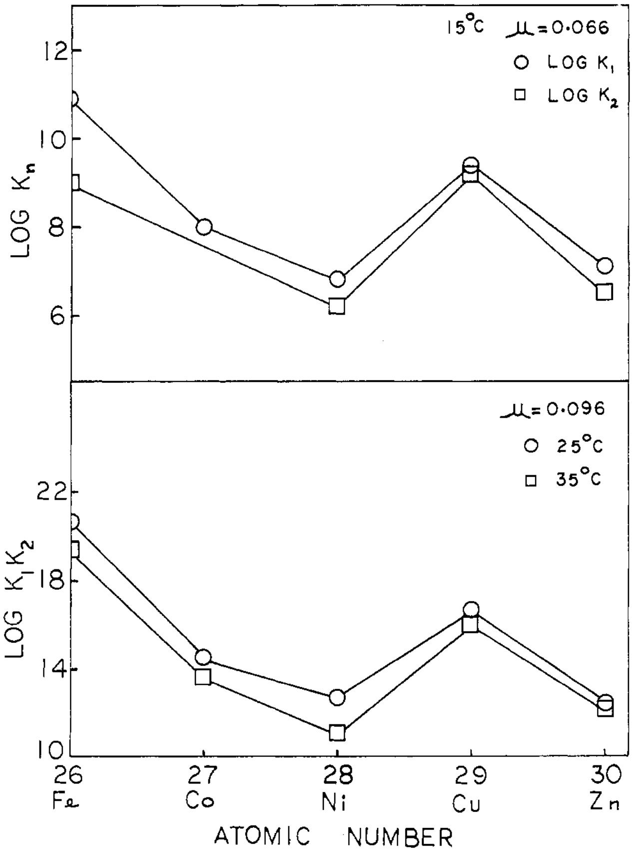


Fig. 4.—Plots of log formation constants of β-furfuraldoximates against atomic number.

Almost all the metals were studied at five different ionic strengths and three different temperatures, except for cobalt, zinc, and lead. For any metal the sequences observed were: (i) $K_n > K_{n+1}$, (ii) K_n decreases with increasing ionic strength, and (iii) K_n decreases with increasing temperature. The plots of log K_1K_2 *vs.* atomic number (Fig. 4), and log K_n *vs.* atomic number (*cf.* Fig. 2) did not follow the Mellor and Maley[14] sequence. According to the Mellor and Maley sequence, log β_n ($\beta_n = K_1K_2\cdots K_n$) should increase progressively from iron(II) to copper(II) and then decrease from copper(II) to zinc(II). In the present studies in all cases log β_n decreases from iron to nickel and then follows the Mellor and Maley sequence. It should be pointed out here that the Mellor and Maley sequence for bivalent metals is also theoretically expected.[15] This anomaly can be explained on the basis of rapid oxidation of iron(II) and cobalt(II) to iron(III) and cobalt(III) by traces of dissolved oxygen as the pH increased. If this happens, the stability constants will increase by several powers of ten. As further evidence, both in the case of iron and cobalt, three-step formation constants could be obtained. In conformity with this explanation the values of the stability constants of iron and cobalt chelates are listed for iron(III) and cobalt(III) in the tables.

The thermodynamic stability constants in Table IV refer to the standard state of zero ion strength in 75% by volume dioxane and 25% by volume water. The implication of this definition of the standard state has been discussed in an earlier section. Therefore, the standard free energy of chelation calculated from these equilibrium constants will differ from the free energy of chelation with respect to infinitely dilute aqueous solution by a quantity which is the partial molar free energy of transfer of the chelate from the infinitely dilute aqueous solution to the binary solvent.

One rather unusual but interesting and significant finding from the present investigation is the large negative entropy of chelation in the case of iron, which, of course, is a consequence of very large negative enthalpy change. A number of possible explanations may be given from the point of view of solvent[16] and ligand field–central ion interaction. Such interpretation will be speculative only until we have magnetic and spectroscopic data.

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(14) D. P. Mellor and L. Maley, *Nature*, **161**, 436 (1948).

(15) L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1961.

(16) H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).