Determination of Thermodynamic Data for Ni(II) Acetylacetonate in Mixed Solvents

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Thermodynamic data for Ni(II) acetylacetonates have been determined in methanol- and 1-propanol–water systems. Further, on the basis of a mathematical model, these thermodynamic functions have been defined and evaluated at constant temperature and constant dielectric constant.

THERMODYNAMIC data for acetylacetone have been determined in mixed solvents (*2*). Since stability constant data for Ni(II) acetylacetonates in mixed solvents at 25° C. had been obtained (*3*), it seemed desirable to extend the temperature range to determine thermodynamic data for Ni(II) acetylacetonates. As had been done with the ligand (*2, 3*), these thermodynamic functions could be separated into terms depending on the temperature and dielectric constant.

EXPERIMENTAL

The experimental procedure and the data obtained at 25° C. for Ni(II) acetylacetonates in methanol- and 1-propanol–water systems have been described (*3*). Additional data for the same systems were obtained at 0° and 40° C. Because of the increased solution viscosity at 0° C., it was necessary to use the electrode system consisting of the Beckman glass electrode No. 40498 with pH range 0 to 11, temperature range −5° to 80° C., and the Beckman sleeve type calomel electrode No. 40463, temperature range −5° to 100° C.

DISCUSSION OF MATHEMATICAL RELATIONS OF THERMODYNAMIC FUNCTIONS

At a constant ionic constant, the thermodynamic functions can be calculated from equilibrium constants expressed in terms of temperature and dielectric constant.

By applying the treatment of Svirbely and Warner (*4*) to the equilibrium constant, one may write

$$\ln K = f(D, T) \qquad (1)$$

The expression for the total differential of ln K with respect to T and D is

$$d \ln K = \left[\frac{\partial \ln K}{\partial D}\right]_T dD + \left[\frac{\partial \ln K}{\partial T}\right]_D dT \qquad (2)$$

Dividing by dT

$$\frac{d \ln K}{dt} = \left[\frac{\partial \ln K}{\partial D}\right]_T \frac{dD}{dT} + \left[\frac{\partial \ln K}{\partial T}\right]_D \qquad (3)$$

Consider the Van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad (4)$$

where ΔH° is the standard heat content change and R is the gas constant. Substituting the term $\Delta H^\circ/RT^2$ into Equation 3,

$$\Delta H^\circ = 2.303\, RT^2 \left[\frac{\partial \log K}{\partial D}\right]_T \frac{dD}{dT} + 2.303\, RT^2 \left[\frac{\partial \log K}{\partial T}\right]_D \qquad (5)$$

where K could be either K_1 or K_2.

ΔH° of a chelation process consists of two heat terms, ΔQ°_T and ΔQ°_D, which are defined by

$$\Delta Q^\circ_T = 2.303\, RT^2 \left[\frac{\partial \log K}{\partial D}\right]_T \frac{dD}{dT} \qquad (6)$$

$$\Delta Q^\circ_D = 2.303\, RT^2 \left[\frac{\partial \log K}{\partial T}\right]_D \qquad (7)$$

The term ΔQ°_T is the standard heat of reaction related to the effect of dielectric constant on the equilibrium constant, while ΔQ°_D is the measure of the effect of temperature on the equilibrium constant. The algebraic sum of the two heat terms gives the net enthalpy of reaction due to changes in both temperature and dielectric constant:

$$\Delta H^\circ = \Delta Q^\circ_T + \Delta Q^\circ_D \qquad (8)$$

To evaluate ΔQ°_T from Equation 6, dD/dT for each solvent composition was interpolated from the data of Akerlöf (*1*). According to Akerlöf

$$\frac{dD}{dT} = -bT \qquad (9)$$

where D is the dielectric constant for any given solvent composition, T is the absolute temperature, and b is an empirical constant. The term

$$\left[\frac{(\partial \log K)}{\partial D}\right]_T$$

is evaluated by differentiating the proper equation found by the method of least squares when log K was plotted *vs.* $1/D$ at a given temperature. The general form of such equations has been found by many investigators to be

$$\log K = m(1/D) + \log K_0 \qquad (10)$$

where log K_0 is the y-intercept and m is the slope of the line. Differentiating with respect to D

$$\left[\frac{\partial \log K}{\partial D}\right]_T = -\left(\frac{m}{D^2}\right) \qquad (11)$$

and substituting Equations 9 and 11 into Equation 6 one has

$$\Delta Q^\circ_T = 2.303\ RT^2\left(\frac{mb}{D}\right) \qquad (12)$$

The determination of ΔQ°_D is simpler since it involves only the evaluation of $(\partial \log K/\partial T)_D$. If one considers the observed relationship between log K and $1/T$ in

$$\log K = m'\ (k/T) + \log K'_0 \qquad (13)$$

where the terms have the same meaning as in Equation 10, differentiation of this equation with respect to temperature at constant dielectric constant yields

$$\left[\frac{\partial \log K}{\partial T}\right]_D = -\left(\frac{m'}{T^2}\right) \qquad (14)$$

which, upon substitution into Equation 7, gives

$$\Delta Q^\circ_D = -2.303\ Rm' \qquad (15)$$

Therefore, if a plot of log K against $1/T$ at constant D has a positive slope, ΔQ°_D will be negative. The sign of ΔH°, then, will depend upon the magnitude of both ΔQ°_T and ΔQ°_D and will be negative only when ΔQ°_D is numerically larger than ΔQ°_T.

Standard free energy change, ΔF°, for the chelation process was evaluated from the equation

$$\Delta F^\circ = -2.303\ RT \log K \qquad (16)$$

The evaluation of the standard entropy of reaction can be subjected to an approach analogous to the evaluation

Table I. Dissociation Constants of Acetylacetone at 0°, 25°, and 40° C.

X_2	$1/D$	$\log 1/\gamma\ 2\pm$	pK'_D	pK_D
		METHANOL-WATER SYSTEM		
		0° C.		
0.000	0.0113	0.09	9.04	9.13
0.098	0.0125	0.11	9.16	9.27
0.220	0.0140	0.13	9.32	9.45
0.289	0.0149	0.14	9.41	9.55
0.374	0.0161	0.16	9.53	9.69
0.474	0.0176	0.17	9.70	9.87
0.590	0.0196	0.20	9.90	10.10
		25° C.		
0.000	0.0127	0.11	8.87	8.98
0.099	0.0142	0.13	9.01	9.14
0.222	0.0160	0.14	9.18	9.32
0.295	0.0172	0.15	9.30	9.45
0.383	0.0186	0.17	9.42	9.59
0.485	0.0205	0.19	9.58	9.77
0.610	0.0230	0.22	9.81	10.03
		40° C.		
0.000	0.0137	0.11	8.76	8.87
0.099	0.0152	0.13	8.89	9.02
0.224	0.0174	0.15	9.08	9.23
0.299	0.0188	0.16	9.19	9.35
0.387	0.0204	0.18	9.32	9.50
0.489	0.0226	0.20	9.50	9.70
0.621	0.0257	0.25	9.77	10.02
		1-PROPANOL-WATER SYSTEM		
		0° C.		
0.000	0.0113	0.09	9.04	9.13
0.056	0.0131	0.12	9.19	9.31
0.132	0.0160	0.17	9.40	9.57
0.183	0.0182	0.21	9.54	9.75
0.251	0.0212	0.26	9.73	9.99
0.334	0.0248	0.33	9.97	10.30
0.450	0.0297	0.42	10.26	10.68
		25° C.		
0.000	0.0127	0.11	8.87	8.98
0.056	0.0149	0.14	9.02	9.16
0.134	0.0183	0.20	9.23	9.43
0.188	0.0213	0.24	9.40	9.64
0.256	0.0247	0.29	9.62	9.91
0.346	0.0294	0.38	9.88	10.26
0.473	0.0352	0.50	10.16	10.66
		40° C.		
0.000	0.0137	0.11	8.76	8.87
0.056	0.0159	0.15	8.93	9.08
0.134	0.0199	0.22	9.13	9.35
0.188	0.0230	0.26	9.32	9.58
0.256	0.0268	0.31	9.51	9.82
0.346	0.0318	0.40	9.77	10.17
0.473	0.0386	0.53	10.08	10.61

Table II. Stability Constants of Ni(II) Acetylacetonate at 0°, 25°, and 40° C.

$1/D$	$\log K'_1$	$\log K'_2$	$\log \beta'$	$\log K_1$	$\log K_2$	$\log \beta$
			METHANOL-WATER SYSTEM			
			0° C.			
0.0113	6.26	4.95	11.21	6.35	5.04	11.39
0.0125	6.46	5.09	11.55	6.57	5.20	11.77
0.0140	6.65	5.22	11.87	6.78	5.35	12.13
0.0149	6.80	5.31	12.11	6.94	5.45	12.39
0.0161	7.10	5.47	12.57	7.26	5.63	12.89
0.0176	7.25	5.58	12.83	7.42	5.75	13.17
0.0196	7.62	5.79	13.41	7.82	5.99	13.81
			25° C.			
0.0127	5.94	4.50	10.44	6.05	4.61	10.66
0.0142	6.24	4.72	10.96	6.37	4.85	11.22
0.0160	6.50	4.92	11.42	6.64	5.06	11.70
0.0172	6.70	5.06	11.76	6.85	5.21	12.06
0.0186	6.90	5.13	12.03	7.07	5.30	12.37
0.0205	7.19	5.31	12.50	7.38	5.50	12.88
0.0230	7.70	5.56	13.26	7.92	5.78	13.70
			40° C.			
0.0137	5.70	4.26	9.96	5.81	4.37	10.18
0.0152	5.96	4.52	10.48	6.09	4.65	10.74
0.0174	6.30	4.67	10.97	6.45	4.82	11.27
0.0188	6.64	4.84	11.48	6.80	5.00	11.80
0.0204	6.90	5.00	11.90	7.08	5.18	12.26
0.0226	7.17	5.20	12.37	7.37	5.40	12.77
0.0257	7.65	5.50	13.15	7.90	5.75	13.65
			1-PROPANOL-WATER SYSTEM			
			0° C.			
0.0113	6.26	4.95	11.21	6.35	5.04	11.39
0.0131	6.45	5.01	11.46	6.57	5.13	11.70
0.0160	6.72	5.28	12.00	6.89	5.45	12.34
0.0182	6.89	5.37	12.26	7.10	5.58	12.68
0.0212	7.13	5.61	12.74	7.39	5.87	13.26
0.0248	7.49	6.01	13.50	7.82	6.34	14.16
0.0297	7.97	6.28	14.25	8.39	6.70	15.09
			25° C.			
0.0127	5.94	4.50	10.44	6.05	4.61	10.66
0.0149	6.05	4.61	10.66	6.19	4.75	10.94
0.0183	6.32	4.80	11.12	6.52	5.00	11.52
0.0213	6.65	5.05	11.70	6.89	5.29	12.18
0.0247	7.03	5.41	12.44	7.32	5.70	13.02
0.0294	7.41	5.71	13.12	7.79	6.09	13.88
0.0352	7.90	6.22	14.12	8.40	6.72	15.12
			40° C.			
0.0137	5.70	4.26	9.96	5.81	4.37	10.18
0.0159	5.85	4.51	10.36	6.00	4.66	10.66
0.0199	6.24	4.67	10.91	6.46	4.89	11.35
0.0230	6.50	4.82	11.32	6.76	5.08	11.84
0.0268	6.75	5.15	11.90	7.06	5.46	12.52
0.0318	7.29	5.61	12.90	7.69	6.01	13.70
0.0386	7.80	5.98	13.78	8.33	6.51	14.84

of ΔH° for a reaction. The term ΔS° is defined in terms of ΔF° and T

$$-\Delta S^\circ = \left[\frac{d(\Delta F^\circ)}{dT}\right]_P \tag{17}$$

The term ΔS° was also separated into two terms, ΔS°_D and ΔS°_T.

The final equations for ΔS°_T, ΔS°_D, and $\Delta S^\circ_{\text{tot}}$ are

$$\Delta S^\circ_T = 2.303\left(\frac{pb}{D}\right) \tag{18}$$

Table V. Standard Free Energies of Dissociation of Acetylacetone in Methanol- and 1-Propanol–Water Systems at 0°, 25°, and 40° C., Kcal. Mole^{-1}

ΔF°, Methanol-Water			ΔF°, 1-Propanol-Water		
0° C.	25° C.	40° C.	0° C.	25° C.	40° C.
11.4	12.3	12.8	11.4	12.3	12.8
11.6	12.5	12.9	11.6	12.5	13.0
11.8	12.7	13.2	11.9	12.8	13.4
11.9	12.9	13.4	12.2	13.1	13.7
12.1	13.1	13.6	12.5	13.5	14.0
12.3	13.3	13.9	12.9	14.0	14.5
12.6	13.7	14.3	13.4	14.6	15.2

Table III. Standard Heat of Dissociation of Acetylacetone in Methanol- and 1-Propanol–Water Systems at 0°, 25°, and 40° C., Kcal. Mole^{-1}

0° C.			25° C.			40° C.		
ΔQ°_T	ΔQ°_D	ΔH°	ΔQ°_T	ΔQ°_D	ΔH°	ΔQ°_T	ΔQ°_D	ΔH°
			METHANOL-WATER					
−2.1	4.7	2.6	−2.5	5.0	2.5	−2.7	5.2	2.5
−2.4	4.9	2.5	−2.8	5.4	2.6	−3.1	5.6	2.5
-2.8	5.2	2.4	−3.4	5.8	2.4	−3.7	6.1	2.4
−3.1	5.5	2.4	−3.7	5.9	2.2	−4.2	6.4	2.2
−3.5	5.8	2.3	−4.2	6.2	2.0	−4.7	6.7	2.0
−4.0	6.3	2.3	−4.8	6.6	1.8	−5.4	7.2	1.8
−4.5	6.6	2.1	−5.5	7.2	1.7	−6.2	7.9	1.7
			1-PROPANOL–WATER					
−1.5	3.9	2.4	−1.8	4.1	2.3	−2.0	4.2	2.2
−1.8	4.2	2.4	−2.2	4.4	2.2	−2.4	4.6	2.2
−2.4	4.5	2.1	−2.9	4.9	2.0	−3.2	5.2	2.0
−2.8	4.9	2.1	−3.5	5.4	1.9	−3.8	5.6	1.8
−3.4	5.3	1.9	−4.2	6.0	1.8	−4.6	6.2	1.6
−4.1	5.9	1.8	−5.3	6.6	1.3	−5.7	6.9	1.2
−5.1	6.6	1.5	−6.6	7.4	0.8	−7.2	7.9	0.7

Table VI. Standard Heats of Chelation of Ni(II) Acetylacetonates in Methanol-Water System at 0°, 25°, and 40° C., Kcal. Mole^{-1}

0° C.			25° C.			40° C.		
ΔQ°_T	ΔQ°_D	ΔH°	ΔQ°_T	ΔQ°_D	ΔH°	ΔQ°_T	ΔQ°_D	ΔH°
			FIRST CHELATION					
3.2	−8.8	−5.6	4.3	−8.8	−4.5	5.0	−8.8	−3.8
3.6	−8.8	−5.2	4.9	−8.9	−4.0	5.7	−8.9	−3.2
4.3	−8.9	−4.6	5.8	−8.9	−3.1	6.9	−8.9	−2.0
4.7	−8.9	−4.2	6.4	−8.9	−2.5	7.7	−9.0	−1.3
5.2	−8.9	−3.7	7.2	−9.0	−1.8	8.6	−9.0	−0.4
6.0	−9.0	−3.0	8.2	−9.0	−0.8	10.0	−9.0	1.0
6.8	−9.0	−2.2	9.4	−9.0	+0.4	11.5	−9.0	2.5
			SECOND CHELATION					
1.9	−8.8	−6.7	2.6	−8.9	−6.3	3.2	−8.9	−5.7
2.2	−8.8	−6.6	3.0	−8.9	−5.9	3.7	−8.9	−5.2
2.6	−8.8	−6.2	3.5	−8.9	−5.4	4.4	−8.9	−4.5
2.8	−8.8	−6.0	3.9	−8.9	−5.0	4.8	−9.0	−4.2
3.2	−8.9	−5.7	4.3	−9.0	−4.7	5.5	−9.0	−3.5
3.6	−8.9	−5.3	5.0	−9.0	−4.0	6.4	−9.0	−2.6
4.1	−8.9	−4.8	5.7	−9.0	−3.3	7.4	−9.0	−1.6

Table IV. Standard Entropy of Dissociation of Acetylacetone in Methanol- and 1-Propanol–Water Systems at 0°, 25°, and 40° C., Cal. Mole^{-1} Deg.$^{-1}$

0° C.			25° C.			40° C.		
ΔS°_T	ΔS°_D	$\Delta S^\circ_{\text{tot}}$	ΔS°_T	ΔS°_D	$\Delta S^\circ_{\text{tot}}$	ΔS°_T	ΔS°_D	$\Delta S^\circ_{\text{tot}}$
				METHANOL-WATER				
−7.8	−24.4	−32.2	−8.3	−24.5	−32.8	−8.7	−23.9	−32.6
−8.8	−24.5	−33.3	−9.5	−23.8	−33.3	−9.9	−23.3	−33.2
−10.4	−24.0	−34.4	−11.2	−23.4	−34.6	−11.9	−22.5	−34.4
−11.4	−23.3	−34.7	−12.4	−23.7	−36.1	−13.2	−22.6	−35.8
−12.7	−23.1	−35.8	−14.0	−23.0	−37.0	−15.0	−22.0	−37.0
−14.5	−22.1	−36.6	−16.0	−22.6	−38.6	−17.2	−20.9	−38.3
−16.5	−22.3	−38.8	−18.4	−21.7	−40.1	−19.9	−20.3	−40.2
				1-PROPANOL-WATER				
−5.5	−27.6	−33.1	−6.1	−27.3	−33.4	−6.3	−27.3	−33.6
−6.7	−28.1	−34.8	−7.5	−27.0	−34.5	−7.6	−26.7	−34.3
−8.7	−27.3	−36.0	−9.9	−26.5	−36.4	−10.2	−26.1	−36.3
−10.3	−26.6	−36.9	−11.9	−25.9	−37.8	−12.3	−25.8	−38.1
−12.4	−26.3	−38.7	−14.3	−25.1	−39.4	−14.8	−25.2	−40.0
−15.1	−25.5	−40.6	−17.6	−24.8	−42.4	−18.3	−24.0	−42.3
−18.8	−24.9	−43.7	−22.1	−23.9	−46.0	−23.2	−23.2	−46.4

Table VII. Standard Heats of Chelation of Ni(II) Acetylacetonate in 1-Propanol-Water System at 0°, 25°, and 40° C., Kcal. Mole^{-1}

0° C.			25° C.			40° C.		
ΔQ°_T	ΔQ°_D	ΔH°	ΔQ°_T	ΔQ°_D	ΔH°	ΔQ°_T	ΔQ°_D	ΔH°
FIRST CHELATION								
2.0	−7.8	−5.8	2.6	−7.9	−5.3	3.0	−8.0	−5.0
2.4	−7.9	−5.5	3.2	−8.1	−4.9	3.6	−8.2	−4.6
3.1	−8.2	−5.1	4.2	−8.3	−4.1	4.8	−8.4	−3.7
3.7	−8.3	−4.6	5.1	−8.5	−3.4	5.7	−8.7	−3.0
4.5	−8.6	−4.1	6.1	−8.8	−2.7	6.9	−8.9	−2.0
5.4	−8.8	−3.4	7.6	−9.1	−1.5	8.5	−9.3	−0.8
6.7	−9.0	−2.3	9.5	−9.6	−0.1	10.9	−9.9	1.0
SECOND CHELATION								
1.7	−8.0	−6.3	2.3	−8.1	−5.8	2.5	−8.2	−5.7
2.1	−8.2	−6.2	2.8	−8.3	−5.5	3.0	−8.4	−5.4
2.7	−8.4	−5.7	3.7	−8.6	−4.9	4.0	−8.7	−4.7
3.2	−8.6	−5.4	4.5	−8.8	−4.3	4.8	−9.0	−4.2
3.8	−8.8	−5.0	5.4	−9.1	−3.7	5.9	−9.2	−3.3
4.6	−9.1	−4.5	6.7	−9.5	−2.8	7.2	−9.6	−2.4
5.8	−9.4	−3.6	8.4	−9.9	−1.5	9.2	−10.0	−0.8

Table VIII. Standard Free Energies of Chelation of Ni(II) Acetylacetonate in Methanol- and 1-Propanol–Water Systems at 0°, 25°, and 40° C., Kcal. Mole^{-1}

ΔF°, First Chelation			ΔF°, Second Chelation		
0° C.	25° C.	40° C.	0° C.	25° C.	40° C.
METHANOL-WATER					
−7.9	−8.3	−8.4	−6.4	−6.4	−6.4
−8.2	−8.6	−8.8	−6.6	−6.6	−6.6
−8.5	−9.1	−9.3	−6.8	−6.9	−6.9
−8.7	−9.3	−9.7	−6.9	−7.0	−7.2
−9.0	−9.7	−10.0	−7.0	−7.2	−7.4
−9.3	−10.1	−10.6	−7.2	−7.5	−7.8
−9.7	−10.7	−11.4	−7.5	−7.9	−8.2
1-PROPANOL–WATER					
−7.9	−8.2	−8.3	−6.2	−6.2	−6.3
−8.2	−8.5	−8.6	−6.4	−6.5	−6.5
−8.6	−9.0	−9.2	−6.8	−6.9	−7.0
−8.9	−9.4	−9.7	−7.0	−7.3	−7.4
−9.3	−9.9	−10.2	−7.4	−7.7	−7.9
−9.8	−10.6	−10.9	−7.8	−8.4	−8.5
−10.4	−11.4	−11.9	−8.4	−9.1	−9.3

Table IX. Standard Entropies of Chelation of Ni(II) Acetylacetonate in Methanol-Water System at 0°, 25°, and 40° C., Cal. Mole^{-1} Deg.$^{-1}$

0° C.			25° C.			40° C.		
ΔS°_T	ΔS°_D	ΔS°_{tot}	ΔS°_T	ΔS°_D	ΔS°_{tot}	ΔS°_T	ΔS°_D	ΔS°_{tot}
FIRST CHELATION								
11.8	−3.4	8.4	14.4	−1.6	12.8	16.0	−1.3	14.7
13.4	−2.4	11.0	16.5	−1.1	15.4	18.3	−0.4	17.9
15.7	−1.4	14.3	19.5	+0.6	20.1	22.0	+1.3	23.3
17.1	−0.6	16.5	21.6	+1.2	22.8	24.5	+2.4	26.9
19.2	+0.2	19.4	24.3	+2.2	26.5	27.6	+3.1	30.7
21.9	+1.2	23.1	27.8	+3.4	31.2	31.8	+5.0	37.0
25.0	+2.5	27.5	31.8	+5.4	37.2	36.8	+7.5	44.3
SECOND CHELATION								
7.1	−8.9	−1.8	8.7	−8.4	0.3	10.2	−8.0	2.2
8.1	−8.3	−0.2	9.9	−7.6	2.3	11.7	−7.2	4.5
9.5	−7.6	1.9	11.7	−6.7	5.0	14.0	−6.3	7.7
10.4	−7.1	3.3	13.0	−6.3	6.7	15.6	−6.0	9.6
11.6	−6.9	4.7	14.6	−6.2	8.4	17.7	−5.2	12.5
13.3	−6.2	7.1	16.7	−5.0	11.7	20.3	−3.7	16.6
15.1	−5.2	9.9	19.1	−3.7	15.4	23.5	−2.4	21.1

Table X. Standard Entropies of Chelation of Ni(II) Acetylacetonate in 1-Propanol–Water System at 0°, 25°, and 40° C., Cal. Mole^{-1} Deg.$^{-1}$

0° C.			25° C.			40° C.		
ΔS°_T	ΔS°_D	ΔS°_{tot}	ΔS°_T	ΔS°_D	ΔS°_{tot}	ΔS°_T	ΔS°_D	ΔS°_{tot}
FIRST CHELATION								
7.3	0.4	7.7	8.8	0.8	9.6	9.4	0.9	10.3
8.8	1.0	9.8	10.7	1.4	12.1	11.4	1.5	12.9
11.5	1.3	12.8	14.1	2.2	16.3	15.3	2.4	17.7
13.5	2.0	15.5	17.0	3.0	20.0	18.3	3.2	21.5
16.4	2.5	18.9	20.4	3.9	24.3	22.2	4.0	26.2
19.8	3.5	23.3	25.3	5.1	30.4	27.2	5.3	32.5
24.6	5.1	29.7	31.7	6.6	38.3	34.6	6.5	41.1
SECOND CHELATION								
6.2	−6.0	0.2	7.8	−6.5	1.3	7.9	−6.2	1.7
7.5	−6.5	1.0	9.6	−6.2	3.4	9.6	−6.0	3.6
9.8	−6.0	3.8	12.5	−5.7	6.8	12.9	−5.4	7.5
11.6	−5.7	5.9	15.0	−5.0	10.0	15.4	−5.0	10.4
14.0	−5.1	8.9	18.1	−4.5	13.6	18.6	−4.2	14.4
17.0	−4.7	12.3	22.4	−3.8	18.6	23.0	−3.5	19.5
21.1	−3.6	17.5	28.0	−2.5	25.5	29.2	−2.0	27.2

$$\Delta S^\circ_D = \frac{p'}{T^2} \tag{19}$$

$$\Delta S^\circ_{tot} = \Delta S^\circ_T + \Delta S^\circ_D \tag{20}$$

where

$$p = \left[\frac{d(\Delta F^\circ)}{d(1/D)}\right]_T$$

$$p' = \left[\frac{d(\Delta F^\circ)}{d(1/T)}\right]_D$$

The standard entropy of reaction, ΔS°_{tot}, may also be calculated from the expression;

$$-\Delta S^\circ_{tot} = \frac{\Delta F^\circ - \Delta H^\circ}{T} \tag{21}$$

The values of ΔS°_{tot} calculated by using Equations 20 and 21 agreed within the limits of experimental error. The dissociation constant of acetylacetone and the stability constants of Ni(II) acetylacetonates were determined as described (*3, 4*) and are given in Tables I and II. The thermodynamic functions for the dissociation of acetylacetone and the chelates of Ni(II) acetylacetonates were calculated according to the above procedure and are given in Tables III through X. The heat terms, ΔQ°_T, ΔQ°_D, and ΔH° are reliable to ±150, ±150, and ±300 cal. per mole, respectively. The values for ΔS°_T, ΔS°_D, and ΔS°_{tot} are reliable to ±0.30, ±0.3, and ±0.60 e.u.

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RECEIVED for review March 29, 1967. Accepted December 26, 1967. Presented at the International Congress of Polarography, Kyoto, Japan, 1966. Work supported by the Atomic Energy Commission under Contract No. AT(30-1)3675.