767. *The Heats of Formation of Complex Ions containing Bipyridyl*

By R. L. Davies and K. W. Dunning

A twin microcalorimeter has been used to measure the heats of formation of complex ions of bipyridyl with the bivalent cations of manganese, iron, cobalt, nickel, copper, and zinc in aqueous and ethanolic solutions. By using various proportions of bipyridyl to metal, the heats of formation have been obtained as a function of the degree of formation of the complex system.

The stability constants of these complexes have been measured, using nitrates, under the same conditions of temperature, concentration, and ionic strength as in the calorimetric determinations. Free-energy changes have been calculated from the stability constants and combined with the heats of formation to evaluate the entropy changes in complex formation.

The heat formation of $Fe(bipy)_3^{2+}$, which at 30·3° and in 1M-potassium nitrate is 28 ± 0·3 kcal./mole, is much larger than the heat of formation of $Fe\,en_3^{2+}$. The addition of a third molecule of bipyridyl to Cu(II) involves a smaller enthalpy change than do the first and second steps but this molecule is held relatively more firmly than a third ethylenediamine molecule. In 1M-potassium nitrate at 30·3° the heat of formation of $Cu(bipy)_3^{2+}$ is 21·6 ± 0·3 kcal./mole.

The heats of formation of $M(bipy)_3^{2+}$ from aqueous solutions of bipyridyl and the transition-metal bivalent cation have been compared when the anion was chloride, nitrate, perchlorate, and sulphate.

ALTHOUGH several investigators had measured the stability constants of bipyridyl complexes of metals of the first transition series, manganese(II),[1,2] iron(II),[3-7] nickel(II),[8] copper(II),[9-12] and zinc(II),[8,13] and heats of formation had in some cases been calculated from them, no direct calorimetric work had been done on these systems. It seemed desirable to measure directly the heats of formation of bipyridyl complexes, and also their stability constants, at the same temperature and ionic strength and at similar concentrations. This we have done at 30·3° using a background electrolyte of 1M-potassium nitrate and the nitrates of the transition metals. While this work, which was begun in 1960, was in progress, the results of some calorimetric measurements on bipyridyl complexes of manganese(II), nickel(II), copper(II), and zinc(II) at 25° in 1M-sodium perchlorate were

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reported by Atkinson and Bauman.[14] Also, an extensive series of measurements of stability constants of bipyridyl complexes was published by Irving and Mellor.[15] Later, Anderegg [16] reported measurements of stability constants and heats of formation of bipyridyl complexes of manganese(II), iron(II), cobalt(II), nickel(II), and zinc(II) at 20° in 0·1M-sodium nitrate.

We determined the stability constants of the cobalt(II)–, copper(II)–, and zinc(II)–bipyridyl systems by the method of competitive complex formation involving hydrogen ions, first used by Bjerrum.[17] The values of the stability constants were obtained from the formation curve using the approximation method developed by Bjerrum [17] and applied later by Carlson, McReynolds, and Verhoek.[18]

In the calorimetric experiments involving these metals, the pH of the resulting solution in the calorimeter was measured. From this, the degree of formation, $\bar{n}$, of the system and also [L], the free ligand concentration, were calculated. Hence, each calorimetric experiment was represented by a point on the formation curve. These points for cobalt(II), copper(II), and zinc(II) are shown in Figure 1.

The stability constants of iron(II)– and nickel(II)–bipyridyl complexes could not be determined by the Bjerrum method because the complexes are so strong that the hydrogen ion cannot compete effectively with the metal cation for the ligand and hence there is no measurable change in the pH of the solution with variation of the bipyridyl : metal ratio. The formation curves of the bipyridyl complexes of iron(II), nickel(II), and manganese(II), were measured by a partition method first used by Kolthoff *et al.*,[19] for the 1,10-phenanthroline–zinc system, and later by Irving and Mellor [15] for both bipyridyl and phenanthroline complexes.

For the manganese(II)–bipyridyl system the Bjerrum method was unsatisfactory in that the position of the formation curve was found to be dependent on the pH and on the manganese concentration of the starting solution. For example, with increasing starting hydrogen-ion concentration the formation curve was shifted to lower values on the p_{L} axis. This phenomenon is indicative of the formation of hydroxy-complexes. The distribution method is more reliable because a measurement both of the pH and of the free ligand concentration of the aqueous phase is made.

In the calorimetric system we have assumed as an approximation that the system is in a standard state of infinite dilution and have neglected any heats of dilution occurring during the reaction.

Suppose, as a simple example, we consider a reaction in which the ratio of bipyridyl to metal cation is high, so that only the trisbipyridyl complex of the metal is involved. Let the heat contents per mole at infinite dilution of the solvated species H^+, M^{2+}, HL^+, L, ML_3^{2+}, be $H^\circ_{H^+}$, H°_{M}, H°_{HL}, H°_{L}, $H^\circ_{ML_3}$, respectively. If the number of moles of H^+, HL^+, L, and M^{2+} initially in the system be denoted by $n_{H^+,i}$, $n_{HL,i}$, $n_{L,i}$, $n_{M,i}$, respectively, and the number of moles of the species finally in the calorimeter be denoted by $n_{H^+,f}$, $n_{HL,f}$, $n_{L,f}$, $n_{M,f}$, n_{ML_3}, then the experimentally observed heat of reaction, ΔH_{exp}, is given by equation (1)

$$\Delta H_{\text{exp}} = n_{H^+,f}H^\circ_{H^+} + n_{M,f}H^\circ_{M} + n_{HL,f}H^\circ_{HL} + n_{L,f}H^\circ_{L} + n_{ML_3}H^\circ_{ML_3} - n_{H^+,i}H^\circ_{H^+} - n_{M,i}H^\circ_{M} - n_{HL,i}H^\circ_{HL} - n_{L,i}H^\circ_{L} \quad (1)$$

which may be reduced to the relation

$$\Delta H_{\text{exp}} = [(n_{M,f} - n_{M,i})H^\circ_{M} - 3n_{ML_3}H^\circ_{L} + n_{ML_3}H^\circ_{ML_3}] + (n_{HL,f} - n_{HL,i})\Delta H_{\text{ion}} \quad (2)$$

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where $\Delta H_{\text{ion}} = H^{\circ}_{\text{HL}} - H^{\circ}_{\text{H}^+} - H^{\circ}_{\text{L}}$, $-\Delta H_{\text{ion}}$ being the heat of dissociation per mole of bipyridylium ion at infinite dilution. The terms in the first bracket are the heat of formation of n_{ML_3} moles of tris-complex. Let this be called ΔH_{c}.

Substituting in the second bracket for $n_{\text{HL},f}$ and $n_{\text{HL},i}$ in terms of n_{T}, the total number of moles of bipyridyl in the system (in all states of combination), and $[\text{H}^+]_i$, the initial hydrogen-ion concentration of the solution in the calorimeter, and $[\text{H}^+]_f$, the final hydrogen-ion concentration of the solution in the calorimeter, we obtain equation (3)

$$\Delta H_{\text{exp}} = \Delta H_{\text{c}} + \left\{\frac{(n_{\text{T}} - 3n_{\text{ML}_3})[\text{H}^+]_f}{K_{\text{a}} + [\text{H}^+]_f} - \frac{n_{\text{T}}[\text{H}^+]_i}{K_{\text{a}} + [\text{H}^+]_i}\right\}\Delta H_{\text{ion}} \qquad (3)$$

The term $(n_{\text{HL},f} - n_{\text{HL},i})\Delta H_{\text{ion}}$ is small but not negligible and an estimate of this was made by measuring the pH of the solution in the calorimeter before and after the reaction.

EXPERIMENTAL

Reagents.—Supplies were obtained from G. F. Smith Chemical Co., L. Light and Co., and British Drug Houses Ltd. Bipyridyl was recrystallised from petroleum ether (60—80°) and (40—60°).

Chloroform and n-hexane (May and Baker Ltd.) were dried and fractionated by three distillations. The transition metals, their oxides, nitrates, sulphates, and chlorides were Johnson Matthey " Spectroscopically Pure " samples. All the other reagents were of AnalaR quality.

Absorption spectra were measured with a Unicam S.P. 500 spectrophotometer using silica cells and a cell compartment thermostat-controlled at 30·3°.

Acid Dissociation Constant of the Bipyridylium Ion.—Portions (50 ml.) of a solution of bipyridyl (0·03M) in 1M-potassium nitrate were titrated potentiometrically with 0·1M-nitric acid using a glass electrode which had been standardised with phthalate buffer pH 4. The dissociation constant was estimated by three methods: (*a*) the pH at half neutralisation, (*b*) calculation of pK_{a} for different values of the pH from the equation pK_{a} = pH + log [Hbipy$^+$]/

TABLE 1

Variation of the pH of a solution of 1M-potassium nitrate containing zinc nitrate with the volume of added 2,2′-bipyridyl at 30·3°

V *	pH	$\bar{n}_{\text{H}}$	10^4C_{M}	10^5C_{H}	10^4C_{L}	$\bar{n}$	10^5[L]	pL
0	4·005	0·8060	3·051	9·890	0	0	0	
0·116	4·027	0·7959	3·044	9·863	0·6967	0·209	0·1254	5·90
0·220	4·054	0·7856	3·038	9·843	1·316	0·390	0·2761	5·55
0·310	4·080	0·7754	3·052	9·825	1·850	0·546	0·4167	5·38
0·400	4·106	0·7648	3·027	9·807	2·383	0·702	0·6069	5·22
0·520	4·154	0·7444	3·020	9·784	3·091	0·900	0·9512	5·02
0·602	4·188	0·7293	3·015	9·768	3·573	1·04	1·219	4·91
0·720	4·242	0·7059	3·008	9·746	4·263	1·23	1·690	4·77
0·806	4·291	0·6792	3·003	9·729	4·764	1·36	2·183	4·66
0·900	4·342	0·6538	2·997	9·711	5·310	1·51	2·733	4·56
1·020	4·420	0·6120	2·990	9·688	6·004	1·69	3·731	4·42
1·104	4·480	0·5788	2·985	9·672	6·487	1·81	4·629	4·34
1·205	4·547	0·5408	2·979	9·653	7·067	1·95	5·785	4·24
1·320	4·628	0·4943	2·972	9·631	7·724	2·10	7·444	4·13
1·406	4·701	0·4524	2·967	9·615	8·213	2·20	9·226	4·04
1·500	4·766	0·4157	2·962	9·598	8·746	2·31	11·09	3·96
1·620	4·860	0·3642	2·955	9·575	9·424	2·43	14·31	3·84
1·720	4·932	0·3267	2·949	9·557	9·986	2·52	17·29	3·76
1·800	4·993	0·3269	2·945	9·542	10·44	2·57	20·22	3·69
1·906	5·059	0·2659	2·939	9·523	11·03	2·65	23·88	3·62
2·000	5·116	0·2411	2·934	9·505	11·55	2·70	27·51	3·56
2·120	5·181	0·2148	2·927	9·483	12·21	2·77	32·26	3·49
2·204	5·230	0·1964	2·922	9·468	12·68	2·79	36·33	3·44
2·300	5·276	0·1802	2·917	9·451	13·21	2·83	40·59	3·39
2·408	5·324	0·1644	2·911	9·431	13·80	2·87	45·52	3·34
2·500	5·366	0·1516	2·906	9·415	14·30	2·88	50·25	3·30
2·620	5·411	0·1388	2·899	9·393	14·95	2·92	55·88	3·15

* Volume of added 0·03M-bipyridyl (ml.).

TABLE 2

Degree of formation of cobalt(II) and copper(II) complexes of bipyridyl at 30·3° in in 1M-potassium nitrate

Cobalt:	10^4C_L 0·65—9·9; 10^4C_M 3·00—2·909; 10^4C_H 1·352—1·307; pH 3·869—4·472									
$\bar{n}$	0·204	0·383	0·606	0·745	0·957	1·01	1·36	1·56	1·68	1·85
pL.........	6·29	6·12	5·81	5·73	5·59	5·46	5·39	5·30	5·17	5·05
$\bar{n}$	2·05	2·19	2·37	2·49	2·65	2·74	2·86			
pL.........	4·95	4·86	4·72	4·62	4·47	4·34	4·16			
Copper:	10^4C_L 2·98—14·85; 10^4C_M 2·980—2·861; 10^5C_H 6·833—6·560; pH = 4·174—5·614									
$\bar{n}$	0·994	1·23	1·39	1·56	1·77	1·88	2·03	2·12	2·18	2·28
pL.........	6·32	6·03	5·75	5·54	5·22	4·93	4·70	4·32	4·15	3·97
$\bar{n}$	2·33	2·41	2·49	2·51	2·36	2·59	2·68	2·73	2·78	
pL.........	3·86	3·77	3·66	3·60	3·52	3·47	3·36	3·28	3·20	

[bipy], and (*c*) from a plot of log $[H^+]$ against log $\alpha_1/(1 - \alpha_1)$ where α_1 is the fraction of bipyridyl in the form Hbipy$^+$. The average value obtained from all methods at 30·3° was $pK_a = 4·62$; $\beta_1{}^H = 4·15 \times 10^4$.

Determination of Partition Coefficients.—The procedure employed was that of Irving and Mellor.[15] For the distribution of bipyridyl between aqueous 1M-potassium nitrate and n-hexane at 30·3° the average value of the partition coefficient, p_L, obtained from fourteen experiments was 7·56. The root mean square deviation was 0·3 (Irving and Mellor [15] obtained 9·6 ± 0·2 at 25° and ionic strength 0·1).

For chloroform the average value of p_L obtained from seven experiments was 317 with a root mean square deviation of 13 (Irving and Mellor [15] quote 315 ± 12 at 25°).

Measurements of Metal Stability Constants.—(a) *Potentiometric titration.* To a 50 ml.-portion of a solution which contained zinc nitrate ($3·05 \times 10^{-4}$M), potassium nitrate (1M), and nitric acid (*ca.* 1×10^{-4}M), bipyridyl solution (3×10^{-2}M) was added in 0·1 ml.-portions. The pH of the solution was observed after each addition, using a glass electrode. The total concentration of dissociable hydrogen in the system was taken to be the measured hydrogen-ion concentration of the solution before any bipyridyl had been added. The values obtained for $\bar{n}_H$, $\bar{n}$, and p_L are given in Table 1 and the formation curve of the zinc–bipyridyl system is shown in Figure 1. The stability constants were obtained from the formation curve by the method of Carlson, McReynolds, and Verhoek.[18]

The formation curves of the bipyridyl complexes of cobalt(II) and copper(II) were obtained similarly by pH measurements and are shown in Figure 1. The corresponding values of $\bar{n}$ and pL are given in Table 2.

(b) *Distribution between aqueous solutions and organic solvents.* The formation curves were obtained using the method of ref. 15. Table 3 shows the results for the distribution of bipyridyl between aqueous ferrous nitrate and n-hexane. The formation curve is shown in Figure 1.

For nickel(II) nitrate solutions, points on the formation curve corresponding to $0·3 < \bar{n} < 2·0$ were obtained by using chloroform. Hexane was used to obtain values of $\bar{n} > 2·0$. The results are shown in Table 4.

Points on the formation curve corresponding to $0·2 < \bar{n} < 1·73$ were obtained using hexane and manganese(II) nitrate solution containing nitric acid. It was not possible to obtain higher values of $\bar{n}$ because for higher concentrations of bipyridyl in the hexane layer it was difficult to avoid crystallisation of bipyridyl on the walls of the spectrophotometer cells. Rough values of K_1 and K_2 were calculated from the approximate equations $\log K_1 = \text{pL}\ (\bar{n} = 0·5)$, $\log K_2 = \text{pL}\ (\bar{n} = 1·5)$. The equation defining $\bar{n}$ for the case N = 3 may be written in the form:

$$\bar{n} = \beta_1[L](1 - n) + \beta_2[L]^2(2 - \bar{n}) + \beta_3[L]^3\,(3 - \bar{n}) \qquad (4)$$

When $n = 2$, the term involving β_2 becomes zero. If the value of [L] corresponding in $n = 2$ is obtained by extrapolating the formation curve, and the rough value of β_1 is used, equation (4) may be solved for β_3. Further successive approximations were made improving the values of the stability constants by the Carlson, McReynolds, and Verhoek method.[18]

The values we obtained for the stability constants of the series of metal–pyridyl complexes from manganese(II) to zinc(II) are shown in Table 5 where they are compared with the values obtained by Irving and Mellor [15] and by Anderegg.[16]

The Calorimeter.—The twin microcalorimeter used was of the type developed by Lange,[20] and also by Gucker,[21] and the main construction of the calorimeter was performed by Hyde.[22]

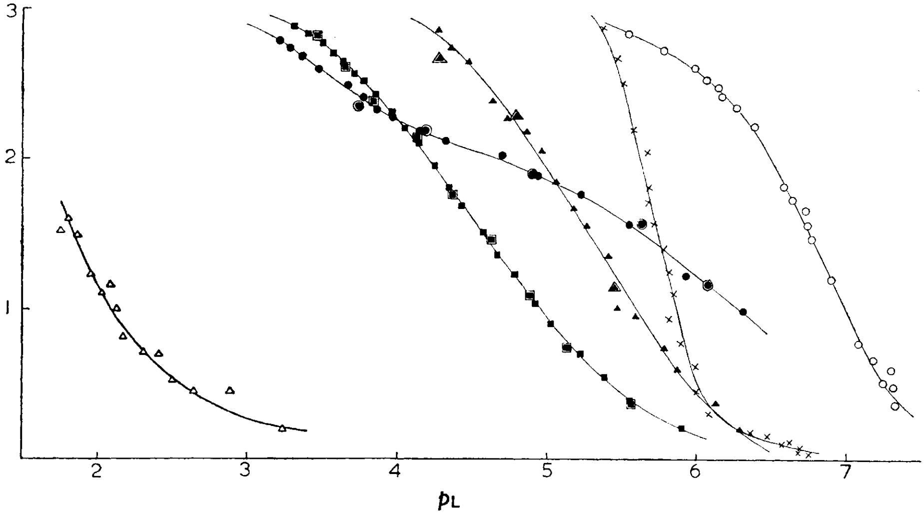

FIGURE 1. Formation curves of bivalent cations with 2,2′-bipyridyl (1M-KNO_3, at 30·3°)

△, Mn; ×, Fe; ▲, Co; ○, Ni; ●, Cu; ■, Zn. Experimental points obtained in the calorimetric systems: ▲, Co; ◉, Cu; ▣, Zn

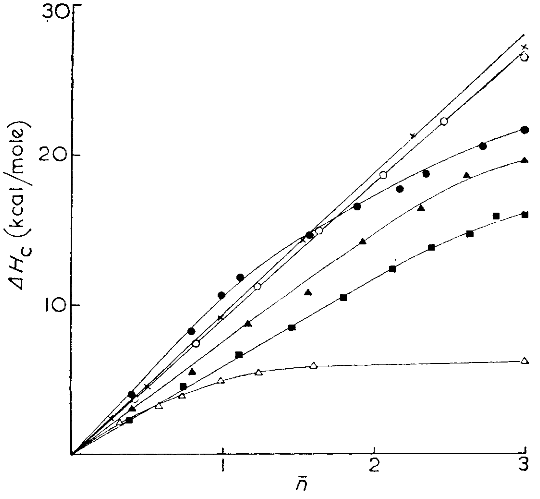

FIGURE 2. Curves of the enthalpy change, ΔH_C, occurring when water molecules in aquated bivalent-metal cations are substituted by bipyridyl as a function of the "ligand number," $\bar{n}$ (1M-KNO_3, 30·3°)

△, Mn; ×, Fe; ▲, Co; ○, Ni; ●, Cu; ■, Zn

The calorimeter was completely immersed in an isothermal bath containing 25 gallons of Shell Dialla oil, the main part of the heating being supplied continuously, independently of the controlling device. The temperature-sensitive elements of the thermoregulator consisted of two fine-gauge nickel wire resistors wound on two glass tubes acting as two arms of a Wheatstone bridge, the other two arms being made up of two "minalpha" wire resistors, all resistors being immersed in the oil bath. The functioning of the thermoregulator depended upon the off-balance potential of the Wheatstone bridge system which was supplied by an alternating

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[21] F. T. Gucker, H. B. Pickard, and R. W. Planck, *J. Amer. Chem. Soc.*, 1939, **61**, 459.

[22] B. Hyde, Ph.D. Thesis, University of Bristol, 1961.

TABLE 3

Distribution of 2,2′-bipyridyl between aqueous iron(II) nitrate (1M-KNO_3) and n-hexane at 30·3°

$10^4C_{\rm M}$	$10^4C_{\rm L}$	D_1	$10^5[{\rm L}]_0$	pH	10^5y	$\bar{n}$	pL	D_2	$10^{-4}K_1$	$10^{-17}\beta_3$
61·53	2·400	0·039	0·133	3·960	0·230	0·039	6·75	0·270 *	4·54	
61·53	3·200	0·046	0·157	3·959	0·272	0·052	6·68	0·375 *	4·34	
61·53	4·800	0·045	0·154	4·050	0·249	0·078	6·69	0·120	4·66	
61·53	6·400	0·059	0·203	3·961	0·375	0·103	6·57	0·162	4·29	
61·53	8·000	0·053	0·181	4·044	0·295	0·130	6·62	0·207	5·06	
61·53	9·600	0·095	0·259	4·000	0·435	0·155	6·47	0·252	3·40	
61·53	11·20	0·096	0·331	3·996	0·558	0·181	6·36	0·295	3·15	
6·153	1·969	0·183	0·631	3·962	1·09	0·302	6·08			
6·153	2·953	0·219	0·755	3·980	1·28	0·459	6·00			
6·153	3·938	0·247	0·852	4·066	1·37	0·618	5·95			
6·153	4·922	0·278	0·959	3·981	1·64	0·773	5·89			
6·153	5·906	0·270	0·931	4·044	1·52	0·935	5·91			
6·153	6·890	0·253	0·872	3·960	1·51	1·10	5·94			
6·153	7·875	0·339	1·17	3·956	2·03	1·25	5·81			
6·153	8·860	0·370	1·28	3·978	2·18	1·40	5·77			
6·153	9·844	0·346	1·19	4·040	1·95	1·57	5·80			
6·153	10·83	0·468	1·61	3·948	2·83	1·71	5·67			
6·153	11·81	0·469	1·61	4·062	2·60	1·81	5·67			
6·153	12·79	0·482	1·66	4·044	2·71	2·04	5·66			
6·153	13·78	0·598	2·06	4·124	3·19	2·19	5·56	0·386		1·36
6·153	15·75	0·699	2·41	4·072	3·85	2·50	5·49	0·438		1·54
6·153	16·74	0·648	2·34	4·304	3·14	2·67	5·53	0·464		1·56
6·153	17·72	0·949	3·27	4·320	4·57	2·81	5·36	0·471		1·05

D_1 = Mean optical density measured at 282 (hexane) mμ (2 cm. cells) (ε 14,500). $p_{\rm L} = [{\rm L}]_0/[{\rm L}] = 7{\cdot}56$. $y = [{\rm L}]_0\left(\frac{1}{p_{\rm L}} + \frac{[{\rm H}^+]}{p_{\rm L}K_{\rm a}} + 1)\right)$. $K_{\rm a} = 2{\cdot}409 \times 10^{-5}$. D_2 = Mean optical density measured at 523 (aqueous layer) mμ (1 mm. cells) except * (5 mm. cells) (ε 8549).

TABLE 4

Degree of formation of nickel(II) and manganese(II) complexes of bipyridyl at 30·3° in 1M-potassium nitrate

Nickel: $10^4C_{\rm L}$ 2·4—17·6; $10^4C_{\rm M}$ 6·115

$\bar{n}$	0·367	0·484	0·518	0·600	0·669	0·778	0·934	1·21	1·29	1·48	1·57	1·66
pL......	7·324	7·324	7·247	7·309	7·180	7·076	7·043	6·896	6·854	6·762	6·730	6·722
$\bar{n}$	1·74	1·82	2·22	2·35	2·41	2·48	2·54	2·60	2·72	2·84		
pL......	6·627	6·569	6·377	6·254	6·153	6·137	6·052	5·972	5·768	5·524		

Manganese: $10^2C_{\rm L}$ 0·8—20·4; $10^2C_{\rm M}$ 1·046

$\bar{n}$	0·200	0·451	0·446	0·525	0·696	0·708	0·816	0·998	1·16	1·10	1·23	1·46
pL......	3·233	2·885	2·645	2·498	2·403	2·306	2·168	2·122	2·078	2·027	1·948	1·904
$\bar{n}$	1·49	1·60	1·73									
pL......	1·856	1·802	1·740									

voltage of 6 volts. The off-balance potential was fed on to the grid of the first valve of an amplifying circuit which supplied the current to a Sunvic relay vacuum switch.

The construction of the two calorimeter vessels is shown in Figure 3. These were mounted side-by-side in a frame below the lid of the thermostat, the various instruments in each vessel being similarly disposed and arranged as exact mirror images about the plane separating them. Each calorimeter contained (*a*) one junction of a calorimeter–calorimeter thermel, (*b*) one junction of a calorimeter-bath thermel, (*c*) an electrical heater, (*d*) a stirrer, and (*e*) an arrangement for initiating reaction.

(a) *The calorimeter–calorimeter thermel.* This was a multijunction thermocouple with one set of junctions in one calorimeter and the other set in the other calorimeter. It recorded the difference in temperature between the two calorimeters, the calorimeter which was not being thermally disturbed acting as a " cold junction " for the thermel. The thermel was composed of 40 s.w.g. copper and 24 s.w.g. constantan wires all double silk covered and painted with shellac after the 90 junctions had been made (giving a 45-junction thermel). The two copper leads to the " end " junctions were made of heavier copper wire (24 s.w.g.) and were about 3 m.

TABLE 5

Stability constants of bivalent cations with 2,2′-bipyridyl

Method *	I	T	pK_a	log K_1	log K_2	log β_2	log K_3	log β_3	Ref.
Manganese									
gl.	0·1M-NaNO$_3$	20	4·49	2·6					16
dist.	0·1M-KCl	25	4·47	2·62	2·00	4·62	1·1	5·6	15
dist.	1M-KNO$_3$	30·3	4·62	2·54	1·85	4·39	1·51	5·9	†
Iron									
sp.	0·1M-NaNO$_3$	20	4·49					17·45	16
dist.	0·1M-KCl	25	4·47	4·20	3·70	7·90	9·55	17·45	15
dist.	1M-KNO$_3$	30·3	4·62	4·65				17·14	†
Cobalt									
m. ex., Hg	0·1M-NaNO$_3$	20	4·49	6·06	5·36	11·42	4·60	16·02	16
dist.	0·1M-KCl	25	4·47	5·65	5·60	11·25	4·80	16·05	15
gl.	1M-KNO$_3$	30·3	4·62	5·72	5·41	11·13	4·80	15·93	†
Nickel									
m. ex., Hg	0·1M-NaNO$_3$	20	4·49	7·13	6·88	14·01	6·53	20·54	16
dist.	0·1M-KCl	25	4·47	7·07	6·86	13·93	6·20	20·13	15
dist.	1M-KNO$_3$	30·3	4·62	6·95	6·83	13·78	6·35	20·13	†
Copper									
l. ex., Hg, m. ex.	0·1M-NaNO$_3$	20	4·49	8·0	5·60	13·60	3·48	17·0	16
dist.	0·1M-KCl	25	4·47	8·15	5·50	13·65	3·30	16·95	15
gl.	1M-KNO$_3$	30·3	4·62	8·39	5·63	14·02	3·63	17·65	†
Zinc									
m. ex., Hg	0·1M-NaNO$_3$	20	4·49	5·3	4·53	9·83	3·80	13·63	16
dist.	0·1M-KCl	25	4·47	5·04	4·35	9·39	3·57	12·96	15
gl.	1M-KNO$_3$	30·3	4·62	5·26	4·55	9·81	3·96	13·77	†

* The abbreviations for methods are: dist. = distribution; m. ex. = metal-ion exchange; gl. = glass electrode; l. ex. = ligand exchange; sp. = spectrophotometric; Hg = mercury electrode. † This Paper. Ref. 15 includes a critical comparison between all measurements reported up to 1962 on the stability of transition-metal complexes with bipyridyl.

long and continued unbroken from their junctions through the lid of the thermostat to the potential-measuring terminals of a Siemens Halske " superior " galvanometer. The averaging or integrating behaviour of the thermel was obtained by varying the relative position of the junctions so that they were spread over a considerable length of the system. A thin tapered glass sheath was used to protect the part of the thermel in the calorimeter, while the exterior part of the thermel was covered by thick Polythene tubing. Good thermal contact between the glass sheath and the thermel junctions was secured by inserting the thermel into the sheath containing molten naphthalene so that no air gap existed when the naphthalene solidified on cooling. The sensitivity of the 45-junction thermel, with a mirror-to-scale distance of 1064 mm., was about 7·0 mm. scale deflection for a temperature difference of 0·001°, *i.e.*, 0·00014°/mm. Hence the temperature difference could be read to about 30 micro-degrees.

(b) *The calorimeter-bath thermel.* This was required mainly to indicate that the temperature of the calorimeters was close to that of the thermostat bath during the reactions occurring in the calorimeters. A multijunction thermocouple was used but not such a sensitive one as for the calorimeter–calorimeter thermel. In each calorimeter there was such a thermel consisting of 20 junctions arranged in a straight stem. The other 20 junctions, subject to the temperature of the thermostat, projected about an inch above the cover of the calorimeter and the wires were left bare in the oil. The entry of the oil into the thermocouple jacket was prevented by sealing the top of the glass sheath with shellac. Only one calorimeter-bath thermel was connected to a galvanometer, so that it recorded the temperature difference between one of the calorimeters and the bath. Hence, in conjunction with the calorimeter–calorimeter thermel, the temperature of both calorimeters with respect to the temperature of the bath could be determined.

(c) *The electrical heater.* This served a dual purpose, being used to bring the temperature of the contents of the calorimeter up to the temperature of the thermostat and to supply electrical calibration heating. The calorimeter heater was made from 40 s.w.g. bright-annealed bare " minalpha " wire which was non-inductively wound on a piece of glass capillary tubing and was insulated and fixed in position by a coating of silicone resin. The connections to this element were of 40 s.w.g. copper wire and outside the calorimeter 25 s.w.g. copper wire was used for connection purposes to give low energy dissipation. The diameter of the glass former was such that when it was covered by the heater element it fitted very closely inside the glass tube which was used as a jacket. This glass jacket was filled to a level just above the heater element with thin oil which provided good thermal contact throughout the heater assembly. The heating element was spread over about one-third of the depth of the calorimeter. By the introduction of dummy heaters, with the same resistance as that of the calorimeter heaters, into the calorimeter heating circuit the current supplied by the lead accumulators did not vary. Two dummy heater resistances were used and these were connected so that the current normally passed through both of them in series but when required could be switched to either of the calorimeter heaters.

(d) *The stirrer.* This was a paddle made from a twisted length of flat glass about 1·5 inches wide to which a B19 ground-glass socket was joined at the bottom. This held a thin-walled fragile glass bulb which was used to hold one of the reagents. The stirrer was attached to a glass tube which was fixed with araldite to a brass sleeve, the latter being attached to the stirrer drive by means of a grub screw. The glass shaft of the stirrer passed up through a glass sleeve which extended from the lid of the calorimeter to a short distance above the level of the oil in the thermostat. One stirrer had a right-hand twist, the other a left-hand twist, both however producing a downward movement of the liquid in the calorimeter, the direction of rotation of the stirrers being symmetrical about the mirror plane. A check on the stirring efficiency was made by placing potassium permanganate in the thin-walled bulb.

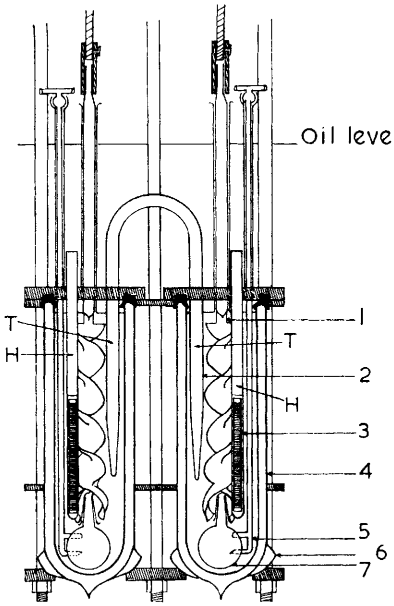

FIGURE 3. Diagram of a twin-micro-calorimeter
1, Stirrer; 2, multijunction thermocouple; 3, calorimeter heater; 4, silvered Dewar vessel; 5, breaker; 6, rubber gasket; 7, thin-walled bulb

(e) *The breaker.* The breaking of fragile glass bulbs containing one of the reactants was used as a convenient means of initiating a reaction. By making the bulbs sufficiently fragile the heat produced on breaking the bulb could be reduced to a very low value. The breaker consisted of a vertical glass rod through the calorimeter lid, with glass sheathing to a level above the oil in the thermostat, located well off the centre axis of the stirrer. At the top two arms were joined at right angles to each other and to the breaker shaft. At the lower end there were attached two curved glass claws ground to points, and when the shaft was rotated by pulling a length of string attached to the top arm of the breaker, the claws impinged on the bulb and broke it. A helical spring returned the arm of the breaker to its zero position.

The calorimeter vessels were two identical silvered Dewar flasks, cylindrical in shape, 10 inches long, 2·5 inches internal diameter, and of about 1-litre capacity. The vacuum jackets of both vessels were opened, re-evacuated, and resealed so that the pressure of gas in both jackets was as nearly the same as possible and small. The calorimeters were sealed by fitting U-shaped Gaco oil rings into circular grooves in a half-inch thick Tufnol plate. The U-shaped seal was located in an inverted position so that the top rim of the Dewar flask fitted between the two lips of the oil seal.

The apparatus could be most conveniently and accurately operated when about 10 calories were liberated during a reaction. The deflection of the Siemens galvanometer was a direct measure of the temperature difference between the two calorimeters and if the system were perfect the deflection would have remained steady until a reaction had been performed, after which it would have assumed another steady position. In practice the deflection of the galvanometer was subject to a steady drift in position due to differences in the leakage moduli of the two calorimeters and to differences in stirring heats. Hence the change in deflection was plotted against time so that extrapolations could be made to determine the true deflection at any given time. The rate of drift of the deflection should be small and constant (usually about 0·2—0·5 mm. per minute) if the apparatus is functioning correctly. A plot was made of the deflections caused, first, by the reaction in one calorimeter, then by a reaction in the other one. This was followed by electrical calibration heatings in succession in the two calorimeters. The electrical heaters were used to generate as nearly as possible the same amount of heat as that produced during the reaction. The values of the voltage and current were recorded from the meters at one-minute intervals to check the constancy of the energy dissipation. The value of the heat generated during the reaction in one of the calorimeters can be calculated by simple proportion from the values of the deflection, D_{R}, produced by the reaction and that, $D_{\mathrm{Calc.}}$, produced by the electrical calibration heating in the same calorimeter. $H_{\mathrm{R}} = D_{\mathrm{R}}vti/D_{\mathrm{Calc.}}J$ where v is the potential difference across the heater, i the current through the heater, and t the time in seconds for which the current was flowing. The value of i contains a correction for the fraction of the current measured by the milliammeter which passes through the voltmeter coil instead of the heater winding.

On the milliammeter scale on the 30mA range, the smallest division corresponds to 0·4 mA and the position of the pointer can be estimated to within one-fifth of one of the small divisions giving an error of ±0·02 mA in a current of 28—30 mA. This corresponds to ±1 in 500. Similarly, the voltmeter gives an error of ±0·002 in 2·8—3·0 volts or ±1 in 1500. The value of the time, t, for which the current was flowing can be estimated to one-fifth of a second at the beginning and end of the heating period of 480—600 seconds, or ±1 in 1200. The absolute accuracy of the stop-watch was checked against 6 p.m. and 10 p.m. Greenwich time signals and found to be 2 seconds slow over this period. This gives an error of 1 in 1220.

Calibration of Calorimeter.—(a) *Heat of neutralisation of hydrochloric acid by sodium hydroxide.* A series of solutions of hydrochloric acid of concentrations in the range 0·05—0·07M were prepared from constant-boiling hydrochloric acid. A portion of hydrochloric acid (9·986 ml.) was placed in each thin-walled glass bulb and attached to the bottom of the stirrer. Sodium hydroxide solution (800 ml.) was placed in the calorimeter vessel. The concentration of sodium hydroxide varied from 0·01 to 0·0016M. The results are shown in Table 6. The average of our values of the heat of neutralisation of hydrochloric acid by sodium hydroxide was 12·86 ± 0·04 kcal./mole at an ionic strength of 0·01 and 30·3°. From a linear extrapolation of Rossini's data[23] the heats of ionisation of water ($\Delta H°$) at 25 and 30° were found to be 13·32 and 13·01 kcal./mole, respectively. The former value is in excellent agreement with the value of 13·33

TABLE 6

Heat of neutralisation of hydrochloric acid by sodium hydroxide at 30·3°

Expt.	10^2C_{NaOH}	10^4n_{HCL}	I	$-\Delta H_{\mathrm{exp}}$ LH	$-\Delta H_{\mathrm{exp}}$ RH	$-\Delta H$
1	1·180	5·017	0·012	6·478	6·450	12·92
2	0·890	6·011	0·009	7·734	7·704	12·85
3	1·102	7·011	0·011	8·984	8·984	12·81
4	0·157	7·011	0·002	9·072	9·011	12·90

n_{HCl} = Number of moles of hydrochloric acid in bulb. I = Ionic strength of final solution in calorimeter. $-\Delta H_{\mathrm{exp}}$ = Heat evolved (cal.) in the right hand or left hand calorimeter. $-\Delta H$ = Average heat of neutralisation in kcal./mole of the two calorimeters.

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[23] F. D. Rossini, *J. Res. Nat. Bur. Stand.*, 1931, **6**, 847.

kcal./mole obtained by direct calorimetric measurements.[24–26] Our value is slightly lower than that predicted from Rossini's data but, since the overall accuracy of the calorimeter is of the order of 1%, the agreement is reasonably good.

(b) *Heat of solution of potassium chloride.* Johnson Matthey " Spectroscopically Pure " potassium chloride was ground into a fine powder using an agate pestle and mortar. The pulverised salt was dried for 2 hr. at 105° and then transferred to a desiccator containing phosphorus pentoxide. About 0·15 g. of the pure dry salt was introduced into each thin-walled dilution bulb by weighing the bulbs before and after addition of the potassium chloride. The calorimeter vessels were filled with freshly distilled water (800 ml.). The results are given in Table 7. At 30·3° the mean heat of solution to a dilution of 1 in 22,000 was +4·13 kcal./mole. This is in good agreement with the values quoted in the literature.[26–34]

TABLE 7

Heat of solution of potassium chloride to a dilution of 1 : 22,000 at 30·3°

			$-\Delta H_{\text{exp}}$		ΔH	
Expt.	W_{LH}	W_{RH}	LH	RH	LH	RH
1	0·1520	0·1506	−8·397	−8·343	4·118	4·130
2	0·1497	0·1505	−8·296	−8·355	4·131	4·138

W_{LH}, W_{RH} = Weight of potassium chloride (g.) in LH and RH bulbs. $-\Delta H_{\text{exp}}$ = Heat evolved (cal.) in calorimeters; ΔH = heat of dilution (kcal./mole).

Heat of Protonation of Bipyridyl.—The heat of formation of the bipyridylium ion was measured by allowing 10 ml. of 0·03M-nitric acid containing 1M-potassium nitrate to react with 800 ml. of 1M-potassium nitrate solution containing bipyridyl. In one experiment the concentration of bipyridyl was 0·001M and in the other 0·03M. The pH of the bipyridyl solution was measured before and after addition of acid. Using the value of K_a for bipyridylium ion as $2{\cdot}409 \times 10^{-5}$ at 30·3°, the number of moles of bipyridylium ion could be calculated. The results are given in Table 8. The mean value of the heat of protonation was 4·02 kcal./mole which is close to the value 3·5 ± 0·5 kcal./mole obtained by Krumholtz [6] from the temperature dependence of K_a.

TABLE 8

Heat of protonation of bipyridyl in 1M-KNO_3 at 30·3°

							$-\Delta H_{\text{exp}}$		
$10^4 C_{\text{L},i}$	$10^4 C_{\text{L},f}$	pH_i	$10^4 n_{\text{HL},i}$	pH_f	$10^4 n_{\text{HL},f}$	$10^4 (n_{\text{HL},f} - n_{\text{HL},i})$	L.H. Cal.	R.H. Cal.	$-\Delta H_{\text{A}}$
10	9·87	6·520	0·09904	4·94	2·610	2·511	1·015	0·965	3·94
300	296·3	7·284	0·5170	6·528	2·917	2·400	1·020	0·950	4·10

The subscripts *i* and *f* refer to the solution initially and finally in the calorimeter. $n_{\text{HL},i}$ = Number of moles of bipyridylium ion in the calorimeter solution initially. $-\Delta H_{\text{exp}}$ = Heat evolved in each calorimeter (cal.). $-\Delta H_{\text{A}}$ = Heat of protonation of bipyridyl (kcal./mole) averaged over the two calorimeters.

Measurements of the Heats of Step-wise Complex Formation of Metal Nitrates with Bipyridyl.—In all experiments on step-wise complex formation an acidified solution of the metallic nitrate (10 ml. delivered from a calibrated pipette) was placed in each of the small thin-walled glass bulbs which were then attached to the ends of stirrers. A fixed volume (800 ml.) of bipyridyl solution was placed in each calorimeter vessel. All solutions of metallic nitrates and

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those of bipyridyl contained 1M-potassium nitrate. Nitric acid was added to the metallic nitrate solutions so that the resulting total nitric acid concentration was 0·01M.

Manganese nitrate and ferrous nitrate solutions were prepared by double decomposition reactions of solutions of barium nitrate with manganese sulphate and ferrous sulphate, respectively. Solutions of cobaltous and nickelous nitrates were made directly from the crystalline nitrates. Cupric nitrate and zinc nitrate solutions were obtained by dissolving cupric oxide and zinc oxide, respectively, in nitric acid. The exact concentration of the metallic ion was determined in each case by standard analytical methods: manganese by ethylenediaminetetra-acetic acid (EDTA) and as manganese pyrophosphate; ferrous iron by permanganate and by dichromate; cobalt by EDTA, mercuric thiocyanate, and an iodometric method; nickel by EDTA and glyoxime; copper by EDTA and as cuprous thiocyanate; and zinc by EDTA.

(a) *Zinc–, copper–, and cobalt–bipyridyl systems.*—The following procedure was adopted for these metals. The pH of the initial bipyridyl solution and the pH of the final solution in the calorimeters were measured. The concentration of bipyridylium ion initially present in the bipyridyl solution before the reaction can be calculated from the pH using the relation $[HL^+]_i = C_{L,i}[H^+]_i/([H^+]_i + K_a)$ where the suffix *i* denotes the initial state of the system in the calorimeter. From the pH of the final solution the degree of formation of the bipyridylium ion may be obtained immediately, since $\bar{n}_H = \beta_1{}^H[H^+]_f/(1 + \beta_1{}^H[H^+]_f)$. The solution of metallic nitrate (10 ml.) was added to 1M-potassium nitrate solution (800 ml.) and the pH was measured. This gave the total hydrogen-ion concentration, C_H, which is what the hydrogen-ion concentration of the system in the calorimeter would have been if no ligand had been added. Then $\bar{n}$, the degree of formation of the metal nitrate–bipyridyl system, was calculated from the relation $\bar{n} = \left\{C_{L,f} - \left(\frac{C_H - [H^+]_f}{\bar{n}_H}\right)\right\}\Big/C_M$. The free ligand concentration, $[L]_f$, could then be obtained from the equation, $[L]_f = (C_{L,f} - \bar{n}C_M)/(1 + \beta_1{}^H[H^+]_f)$. Hence the point on the formation curve corresponding to the state of the system in the calorimeter was obtained. Such points were found to fall on the previously determined formation curves of cobalt–, copper–, and zinc–bipyridyl systems and are shown in Figure 1.

The final concentration of bipyridylium ion in the calorimeter is given by the relation $[HL^+]_f = \bar{n}_H(C_{L,f} - \bar{n}C_M)$, and from this and $[HL^+]_i$, the number of moles of bipyridylium $(n_{HL,f} - n_{HL,i})$, formed as a result of the reaction, can be calculated.

The total heat, ΔH_{exp}, which was measured experimentally and which was due both to the formation of the metallic complexes and to formation of bipyridylium ion (or for low ratios of bipyridyl to metal, in some cases, to dissociation of bipyridylium ion), was thus corrected for

TABLE 9

Calorimetric experiments using varying ratios of bipyridyl to cobalt(II) nitrate ($1M-KNO_3$ at 30·3°)

Expt.	$10^4C_{L,f}$	pH_i	$10^5n_{HL,i}$	pH_f	$10^5n_{HL,f}$	$\bar{n}_H$	$\bar{n}$
1	2·473	6·134	0·5874	4·095			0·399
2	4·970	6·226	0·9536	4·097			0·803
3	7·423	6·282	1·264	4·160	0·9072	0·7417	1·174
4	9·865	6·385	1·335	4·158	0·8837	0·7425	1·569
5	12·332	6·408	1·571	4·276	2·183	0·6874	1·927
6	14·733	6·506	1·521	4·278	2·240	0·6863	2·314
7	17·292	6·600	1·435	4·616	4·510	0·5006	2·611
8	296·3	7·340	4·544	6·892	11·89	0·00529	3

Expt.	$10^5[L]_f$	$10^5\Delta n_{HL}$	$4·02 \times 10^3\Delta n_{HL}$	$-\Delta H_{exp}$	$-\Delta H^*$	$-\Delta H_C$
1	~0·079			1·55		3·09
2	0·199			2·80		5·57
3	0·3890	−0·3568	−0·0143	4·40	4·41	8·78
4	0·3784	−0·4513	−0·0181	5·43	5·45	10·86
5	1·239	0·612	0·0246	7·15	7·13	14·20
6	1·264	0·719	0·0289	8·28	8·25	16·44
7	5·604	3·075	0·1236	9·47	9·35	18·63
8	2707	7·346	0·2953	10·16	9·87	19·66

$10^4C_{M,f} = 6·194$; $10^4n_M = 5·017$ (moles); $10^5C_H = 8·035$ except for Expt. 7 where $10^5C_H = 2·415$; $\Delta n_{HL} = n_{HL,f} - n_{HL,i}$; $-\Delta H_{exp}$ = average heat evolved in the two calorimeters (cal.); $-\Delta H^*$ = corrected heat (cal.); $-\Delta H_C$ = heat of complex formation (kcal./mole Co).

TABLE 10

Calorimetric experiments using varying ratios of bipyridyl to copper(II) nitrate
(1M-KNO_3 at 30·3°)

Expt.	$10^4C_{\mathrm{L},f}$	pH_i	$10^5n_{\mathrm{HL},f}$	pH_f	$10^5n_{\mathrm{HL},f}$	$\bar{n}_{\mathrm{H}}$	$\bar{n}$
1	2·452	6·134	0·5874	4·050		0·7872	0·3958
2	4·900	6·226	0·953	4·050		0·7872	0·7911
3	6·159						0·9943
4	7·350	6·282	1·264	4·042		0·7330	1·187
5	9·854	6·385	1·335	4·094	0·637	0·7790	1·575
6	12·15	6·408	1·571	4·210	2·505	0·7190	1·892
7	14·79	6·508	1·521	4·598	5·507	0·5116	2·174
8	17·26	6·600	1·435	4·979	6·682	0·3035	2·347
9	22·18	6·660	1·611	5·285	7·098	0·1773	2·783
10	296·3	7·340	4·544	6·818	14·12	0·00627	3

Expt.	$10^5[\mathrm{L}]_f$	$10^5\Delta n_{\mathrm{HL}}$	$4·02 \times 10^3\Delta n_{\mathrm{HL}}$	$-\Delta H_{\mathrm{exp}}$	$-\Delta H^*$	$-\Delta H_{\mathrm{C}}$
1	~0·0001			2·02		4·02
2	~0·035			4·14		8·25
3	~0·050			5·34		10·64
4	0·083			5·93		11·81
5	0·223	−0·698	−0·0280	7·12	7·15	14·25
6	1·208	0·934	0·0375	8·34	8·30	16·55
7	6·49	3·986	0·160	9·05	8·89	17·72
8	18·93	5·247	0·211	9·58	9·37	18·68
9	40·70	5·487	0·221	10·55	10·33	20·59
10	2758	9·576	0·384	11·23	10·85	21·62

$10^4C_{\mathrm{M},f} = 6·194$; $10^4n_{\mathrm{M}} = 5·017$ moles; $10^5C_{\mathrm{H}} = 9·29$. The other symbols have the same significance as in Table 9.

TABLE 11

Calorimetric experiments using varying ratios of bipyridyl to zinc(II) nitrate
(1M-KNO_3 at 30·3°)

Expt.	$10^4C_{\mathrm{L},f}$	pH_i	$10^5n_{\mathrm{HL},i}$	pH_f	$10^5n_{\mathrm{HL},f}$	$\bar{n}_{\mathrm{H}}$	$\bar{n}$
1	2·452	6·134	0·5874	3·971	1·038	0·8161	0·3713
2	4·900	6·226	0·9536	4·039	2·352	0·7913	0·7366
3	7·351	6·282	1·264	4·105	3·397	0·7651	1·105
4	9·807	6·385	1·335	4·216	4·839	0·7163	1·458
5	12·15	6·408	1·571	4·376	6·370	0·6358	1·798
6	14·75	6·508	1·521	4·536	7·414	0·5474	2·126
7	17·18	6·600	1·435	4·777	8·414	0·4095	2·379
8	19·64	6·634	1·519	4·972	8·536	0·3069	2·634
9	22·10	6·660	1·611	5·131	9·150	0·2345	2·809
10	296·3	7·157	6·92	6·741	17·05	0·0075	3

Expt.	$10^5[\mathrm{L}]_f$	$10^5\Delta n_{\mathrm{HL}}$	$4·02 \times 10^3\Delta n_{\mathrm{HL}}$	$-\Delta H_{\mathrm{exp}}$	$-\Delta H^*$	$-\Delta H_{\mathrm{C}}$
1	0·2887	0·4506	0·0181	1·16	1·14	2·29
2	0·7670	1·398	0·0561	2·35	2·30	4·60
3	1·286	2·133	0·0857	3·42	3·33	6·68
4	2·366	3·504	0·1408	4·38	4·24	8·50
5	4·504	4·799	0·1930	5·41	5·22	10·47
6	7·574	5·893	0·2368	6·39	6·15	12·34
7	14·97	6·979	0·2805	7·15	6·87	13·78
8	23·80	7·017	0·2820	7·60	7·32	14·69
9	36·81	7·539	0·3005	8·20	7·90	15·86
10	2793	10·03	0·4030	8·36	7·96	15·92

$10^4C_{\mathrm{M},f} = 6·153$; $10^4n_{\mathrm{M}} = 4·984$; $10^4C_{\mathrm{H}} = 1·205$. The other symbols have the same significance as in Table 9.

TABLE 12

Calorimetric experiments using varying ratios of bipyridyl to nickel(II) nitrate
(1M-KNO_3 at 30·3°)

Expt.	$10^4C_{\mathrm{L},f}$	$\bar{n}$	$-\Delta H_{\mathrm{exp}}$	$-\Delta H_{\mathrm{C}}$	Expt.	$10^4C_{\mathrm{L},f}$	$\bar{n}$	$-\Delta H_{\mathrm{exp}}$	$-\Delta H_{\mathrm{C}}$
1	2·462	0·411	1·82	3·75	5	12·367	2·06	9·07	18·66
2	4·934	0·823	3·60	7·412	6	14·776	2·465	10·78	22·20
3	7·396	1·23	5·44	11·20	7	296·3	3·00	13·20	26·48
4	9·846	1·64	7·24	14·92					

$10^4C_{\mathrm{M},f} = 5·995$; $10^4n_{\mathrm{M}} = 4·856$. In expt. 7, $10^4\Delta n_{\mathrm{HL}} = 0·8536$. For expts. 1—6, $\bar{n} \approx C_{\mathrm{L},f}/C_{\mathrm{M}}$, the heat associated with the bipyridyl–bipyridylium system. Tables 9, 10, and 11 record the results for calorimetric experiments on cobalt, copper, and zinc complexes with bipyridyl. Plots of the enthalpy change, $\triangle H_c$, as a function of the " ligand number " are shown for these systems in Figure 2.

(b) *Nickel–bipyridyl systems.* Table 12 gives the heats measured for the reaction of nickel nitrate with bipyridyl solutions of varying concentration. The complexes of nickel with bipyridyl are too strong for the Bjerrum method of competition with hydrogen ions to be used for measuring $\bar{n}$. A comparison of the pH of a solution obtained by adding nickel nitrate solution (10 ml.) to a 1M-potassium nitrate solution (800 ml.) and the pH of the resulting solution in the calorimeter containing bipyridyl also, showed no measurable change in pH, unless the bipyridyl was present in large excess. Hence the term $C_H - [H^+]_f$ in the expression for $\bar{n}$, tends to zero. For nickel, the degree of formation of the complex system was taken as the ratio of the added bipyridyl to the metal ion $C_{L,f}/C_{M,f}$ except for expt. 7 where the latter ratio was 50 : 1 and $\bar{n}$ was assumed to be 3·0. In this experiment only, a correction was made for the amount of bipyridylium ion formed.

(c) *Manganese–bipyridyl system.* An empirical curve was drawn of the degree of formation, $\bar{n}$, of the complex versus the total concentration, C_L, of ligand. This was obtained from the formation curve, $\bar{n}$ – pL, and the relation $C_L = \bar{n}C_M + [HL^+] + [L]$, assuming, as an approximation, that the amount of bipyridylium ion formed during the reaction was equal to the amount of hydrogen ion which would have been obtained by expanding 10 ml. of acidified manganese(II) nitrate solution into 800 ml. of 1M-potassium nitrate. The error due to the uncertainty of $[HL^+]$ is greatest for very low $\bar{n}$ values but over $\bar{n} = 0{\cdot}45$ it is less than 1%. The value of $\bar{n}$ corresponding to a given ratio of total bipyridyl, $C_{L,f}$, to metal, $C_{M,f}$, in the calorimeter, was read off from the empirical curve. The number of moles of bipyridylium ion, Δn_{HL}, formed during the reaction was calculated from the measured pH of the solution using the same equation in the form $C_L = \bar{n}C_M + [HL^+]\{1 + (k_a/[H^+])\}$. Table 13 and Figure 2 show the values of the heats evolved for varying degrees of formation of the system.

TABLE 13

Calorimetric experiments using varying ratios of bipyridyl to manganese(II) nitrate ($1M$-KNO_3 at 30·3°)

Expt.	10^4C_M	$10^4C_L,$	pH_i	$10^5n_{HL},$	pH_f	$10^5n_{HL,f}$
1	6·085	19·75	6·660	1·440	5·888	7·227
2	6·085	39·51	7·749	0·236	6·290	6·092
3	6·262	59·26	6·548	5·579	6·220	10·81
4	6·262	88·89	6·633	6·890	6·352	12·14
5	6·262	118·5	6·622	9·424	6·376	15·39
6	6·262	162·9	6·980	5·712	6·674	10·80
7	6·085	296·0	7·224	5·933	6·913	11·35
8 *	3·0535	298·2	7·224	5·933	7·07	8·222

Expt.	$\bar{n}$	$10^5\Delta n_{HL}$	$4{\cdot}02 \times 10^3\Delta n_{HL}$	$-\Delta H_{exp}$	$-\Delta H^*$	$-\Delta H_C$
1	0·370	5·780	0·232	1·28	1·05	2·12
2	0·575	5·856	0·235	1·86	1·62	3·27
3	0·727	0·250	0·210	2·22	2·01	3·95
4	0·983	5·250	0·210	2·75	2·54	4·99
5	1·24	5·966	0·240	3·02	2·78	5·47
6	1·60	5·088	0·200	3·21	3·01	5·93
7	3	5·420	0·218	3·29	3·07	6·23
8 *	3	2·289	0·092	1·62	1·53	6·22

* 5 ml. Solution of manganese(II) nitrate was used: $10^5C_H = 6{\cdot}592$. $10^4n_M = 4{\cdot}948$ (expts. 1, 2, 7, 8); $10^4n_M = 5{\cdot}072$ (expts. 3—6).

(d) *Iron–bipyridyl.* An approximate value of $\bar{n}$ was obtained by assuming it to be equal to $C_{L,f}/C_{M,f}$. Interpolation from the formation curve gave the value of the free-ligand concentration, $[L]_f$, corresponding to the approximate value of $\bar{n}$. Substituting these values of n and $[L]_f$, together with the measured hydrogen-ion concentration of the final solution in the calorimeter, into the equation $\bar{n} = (C_{L,f} - [L]_f - [L]_f[H^+]_f/K_a)/C_{M,f}$, a better value of $\bar{n}$ was obtained. A repetition of the approximation gave a second improved value of $\bar{n}$ which differed from the first only in the fourth figure.

The visible absorption spectra of $Fe(bipy)^{2+}$ and $Fe(bipy)_3{}^{2+}$ had previously been described by Krumholtz.[6] The species $Fe(bipy)_3^{2+}$ has a maximum at 523 mμ (ε 8500),[3] and a minimum near 435 mμ, whereas the species $Fe(bipy)^{2+}$ has a maximum at 435 mμ (ε 310).

The extinction coefficient of $Fe(bipy)_3^{2+}$ in 1M-potassium nitrate at 30·3° was found to be 8549 at 523 mμ and 2517 at 435 mμ.

The concentration of $Fe(bipy)_3^{2+}$ in the final solution in the calorimeter was obtained by measuring the optical density of the solution at $\lambda = 523$ mμ, where the absorption of $Fe(bipy)_3^{2+}$ is a maximum, and that of $Fe(bipy)^{2+}$ is zero. The absorption at 435 mμ caused by this concentration of $Fe(bipy)_3^{2+}$ was then calculated and compared with the measured absorption at 435 mμ. Even for those experiments where the ratio of bipyridyl to metal ion was small, the measured absorption at 435 mμ agreed within the experimental error with that calculated from the concentration of $Fe(bipy)_2^{3+}$. There was no extra absorption that could be attributed to $Fe(bipy)^{2+}$. Hence, under our experimental conditions, no complex species, other than $Fe(bipy)_3^{2+}$, could be detected in the final solution in the calorimeter. The degree of formation, $\bar{n}'$, calculated from the optical density at 523 mμ, assuming that the only complex species present was $Fe(bipy)_3$, agreed with that obtained by the first method to within 1%.

The heats evolved, in kcal./mole Fe, for various values of $\bar{n}$ are given in Table 14. The

TABLE 14

Calorimetric experiments using varying ratios of bipyridyl to iron(II) nitrate ($1M-KNO_3$ at 30·3°)

Expt.	$10^4C_{L,f}$	pH_i	$10^5n_{HL,i}$	pH_f	$10^5n_{HL,f}$	$10^4C_{M,f}$	$\bar{n}$	$10^5\Delta n_{HL}$	$4{\cdot}02 \times 10^3\Delta n_{HL}$
1	1·566	6·244	0·293	4·066	0·2930	5·984	0·254		
2	2·953	6·074	0·809	3·860	0·4276	5·815	0·497	−0·382	−0·016
3	5·815	6·222	1·144	3·922	0·1548	5·815	0·985	−0·989	−0·035
4	8·716	6·101	2·248	3·784	1·019	5·603	1·530	−1·229	−0·049
5	12·643	6·222	2·488	3·740	1·708	5·501	2·253	−0·78	−0·030
6	296·3	6·982	10·32	6·588	23·89	6·017	3·0	+13·58	+0·543

Expt.	$-\Delta H_{exp}$	$-\Delta H^*$	$-\Delta H_C$	D (cell-path, mm.)	$\bar{n}'$	$-\Delta H_{C,FeL3}$ (a)	$-\Delta H_{C,FeL3}$ (b)	10^4n_M
1	1·17		2·41	0·448 (10)	0·262	28·50	27·57	4·848
2	2·14	2·16	4·59	0·407 (5)	0·491	27·70	28·01	4·710
3	4·28	4·31	9·15	0·165 (1)	0·995	27·86	27·55	4·710
4	6·44	6·49	14·30	0·249 (1)	1·553	28·03	27·56	4·538
5	9·44	9·47	21·24	0·362 (1)	2·309	28·29	27·62	4·456
6	13·77	13·23	27·14	0·518 (1)	3·02	27·14	27·14	4·874

$\bar{n}$ = Degree of formation of the iron-bipyridyl system interpolated from the formation curve. $-\Delta H_C$ = Heat of the substitution reaction (kcal./mole Fe). $\bar{n}'$ = Degree of formation of the iron–bipyridyl system calculated from the optical density, D, at 523 mμ. $-\Delta H_{C,FeL3}$ = Heat of formation of $Fe(bipy)_3^{2+}$ assuming that only the tris-complex is formed at all values of the degree of formation, calculated (*a*) using $\bar{n}$, and (*b*) using $\bar{n}'$.

heat of formation of $Fe(bipy)_3^{2+}$, assuming it to be the only complex species formed, is also given for different values of $\bar{n}$.

Table 15 gives our values for ΔH_c, the heat of the reaction:

$$[M(H_2O)_6^{2+}]_{aq} + n\,bipy_{aq} \longrightarrow [M(bipy)_n(H_2O)_{6-2n}^{2+}]_{aq} + 2nH_2O_{liq} \qquad (5)$$

(n = 1, 2, and 3) for the transition-metal series manganese to zinc in 1M-potassium nitrate at 30·3°. Also given are the values of ΔG corresponding to the formation constants measured at the same ionic strength and temperature.

For nickel (see Figure 2), the plot of ΔH_C against the "ligand number," $\bar{n}$, is a straight line and therefore the heat evolved due to the addition of the three successive ligands is the same. For manganese, cobalt, copper, and zinc, the graph of ΔH_C versus $\bar{n}$ is curved. In these cases the heats evolved in the successive steps have been obtained by an approximation method. On the assumption that for low values of $\bar{n}$, such as 0·4 and below, the only species present were $M(bipy)^{2+}$ and M_{aq}^{2+}, $\Delta H_{C,1}$ was calculated from the graph of ΔH_C versus $\bar{n}$. Then for a value of $\bar{n}$ such as 1·2 it was assumed that only the species $M(bipy)^{2+}$ and $M(bipy)_2^{2+}$ were present, and $\Delta H_{C,2}$ was obtained. $\Delta H_{C,3}$ was read off from the graph at $\bar{n} = 3$, where the ratio of bipyridyl to metal was *ca.* 50 : 1. The graph for cobalt is linear up to about $\bar{n}$ = 1·9, and then

TABLE 15

Thermodynamic data of reaction (1) (n = 1, 2, or 3) at 30·3° and in 1M-potassium nitrate

M^{2+}	n	$-\Delta H_C$	$-\Delta G$	ΔS	$-\Delta H^*_C$	$-\Delta G^*$	ΔS^*	$-\Delta H\dagger_C$	$-\Delta G\dagger$	$\Delta S\dagger$
Mn	1	5·73	3·53	−7·3	3·5	3·5	0·0	4·3	5·53	4·1
	2	6·11	6·10	0					10·69	
	3	6·23	8·19	6·5					15·65	
Fe	3	28·0	23·80	−13·8	31·35	23·4	−27			
Co	1	7·20	7·95	2·5	8·2	8·1	−0·35			
	2	14·40	15·46	3·5	15·2	15·3	0·35			
	3	19·66	22·13	8·1	21·3	21·7	1·4			
Ni	1	8·90	9·65	2·5	9·6	9·6	0	8·03	9·27	4·0
	2	17·80	19·14	4·4	19·0	18·8	−0·7	16·06	18·09	6·8
	3	26·70	27·95	4·1	28·2	27·6	−2·1	24·09	25·19	3·69
Cu	1	10·16	11·64	4·9	11·9	10·7	−4·1	8·33	9·47	3·8
	2	19·02	19·46	1·5	17·3	18·2	3·1	16·66	17·30	2·48
	3	21·62	24·50	9·5	23·8	22·9	−3·1	24·99		
Zn	1	6·25	7·30	3·5	7·1	7·1	0	5·27	6·67	4·7
	2	11·75	13·62	6·2	12·5	13·2	2·4	10·54	12·92	7·97
	3	15·92	19·12	10·6	17·5	18·3	2·7	15·9	18·75	9·55

ΔH and ΔG are given in kcal./mole and ΔS in cal./mole deg.

* Anderegg.[16] † Atkinson and Bauman.[14]

curves away. Hence, the heats for the addition of the first and second ligand were taken to be equal.

The graph of $\Delta H_C - \bar{n}$ for ferrous iron–bipyridyl is a straight line. However, spectrophotometric determination of the concentration of the tris-complex at every experimental point showed that, even for low values of $\bar{n}$, the amount of $Fe(bipy)^{2+}$ or $Fe(bipy)_2{}^{2+}$ was too small to be measured and that, for the conditions obtaining in the calorimeter, the system could be described completely in terms of $Fe_{aq}{}^{2+}$ and $Fe(bipy)_3{}^{2+}$. The heat of formation of the tris-complex was obtained from the slope of the straight-line graph.

Metal–Bipyridyl Systems using Various Anions.—The results of a series of determinations of the heats of formation of trisbipyridyl complexes using nitrates, chlorides, perchlorates, and sulphates in aqueous solution, and also sulphates in aqueous ethanolic solution, are given in Table 16. In the case of nitrates, chlorides, and perchlorates, bipyridyl (800 ml.; 6×10^{-2}M, half-neutralised with the acid corresponding to the anion of the transition-metal salt) was used in the calorimeters. For the sulphates, hydrochloric acid was used to half-neutralise the bipyridyl. The thin-walled bulbs contained 10 ml. of 5×10^{-2}M-metallic nitrate, chloride, or perchlorate solutions to which the corresponding acid had been added so that the resulting acidity was 3×10^{-2}M. In the case of sulphates experiments were done using 5×10^{-2}M-metallic sulphate (10 ml.) containing 3×10^{-2}M-hydrochloric acid and also a series in which the metallic sulphate solution was $2{\cdot}5 \times 10^{-2}$M and was also 3×10^{-2}M in hydrochloric acid.

TABLE 16

Heats of formation ($-\Delta H$ kcal./mole) of trisbipyridyl complexes at 30·3° of some bivalent transition-metal cations associated with different anions

M^{2+}	MCl_2 (HCl)	$M(NO_3)_2$ (HNO_3)	$M(NO_3)_2$ (HNO_3, 1M-KNO_3)	$M(ClO_4)_2$ ($HClO_4$)	MSO_4 * (HCl, ethanol)	MSO_4 (HCl)	MSO_4 * (HCl)
Ca ...	0·22	0·15	0·17				
Mn ...	4·69	4·60	5·61	4·74	4·96	5·82	5·87
Fe ...	26·00	27·03	27·40	27·25	24·55	24·95	24·83
Co ...	19·10	18·26	18·72	18·66	22·01	19·30	19·54
Ni ...	26·00	25·68	27·24	25·17	27·62	25·19	25·03
Cu ...	21·32	20·95	21·24	20·96	22·24	21·04	21·08
Zn ...	15·40	14·81	15·53	15·17	17·56	15·24	14·56

$10^4 n_M = 5$ except * where $10^4 n_M = 2{\cdot}5$.

When half-neutralised bipyridyl solutions are used, determination of the pH of the solution before and after the reaction does not give an accurate value of the number of moles of bipyridylium ion formed because the buffer capacity of such solutions is a maximum and the pH changes are correspondingly small. Hence, the correction subtracted from the experimental values of the heat of reaction for the nitrates, chlorides, and perchlorates was that heat evolved when 10 ml. of 3×10^{-2}M-acid reacted with 800 ml. of 6×10^{-2}M-half-neutralised bipyridyl solution. In the case of the sulphates the correction was obtained by measuring the heat evolved when 10 ml. of 3×10^{-2}M-hydrochloric acid containing cæsium sulphate (5×10^{-2}M and $2{\cdot}5 \times 10^{-2}$M, respectively) was allowed to react with 800 ml. of 6×10^{-2}M-half-neutralised bipyridyl. The heat corrections were larger for sulphates on account of the heat of dissociation of the hydrogen sulphate ion. The heat corrections (in calories) were as follows: HCl, 0·81; HNO_3, 0·83; $HClO_4$, 0·79; HCl–Cs_2SO_4 ($2{\cdot}5 \times 10^{-2}$M), 1·38; HCl–Cs_2SO_4 (5×10^{-2}M), 1·62; HCl–Cs_2SO_4 ($2{\cdot}5 \times 10^{-2}$M) in 50% ethanol–water, 1·73.

DISCUSSION

In Figure 4 our results for the successive heats of formation of bipyridyl complexes are compared with the heats of formation of ethylenediamine complexes of the same series of metals. The values quoted for ethylenediamine complexes are those of Poulsen and Bjerrum[35] and Ciampolini *et al.*[36] For manganese, iron, and cobalt, the values quoted are for the metal(II)–ethylenediamine systems in 1M-potassium chloride at 25°. In the case of copper, nickel, and zinc the values are for systems in 1M-potassium nitrate. These are more comparable with the present work and we have quoted these in preference to those for the same metals in potassium chloride. Also, since we were unable, by our method, to obtain $\Delta H_{C,1}$ and $\Delta H_{C,2}$ for ferrous–bipyridyl, we have used the values of Baxendale and George,[7] who used ferrous sulphate.

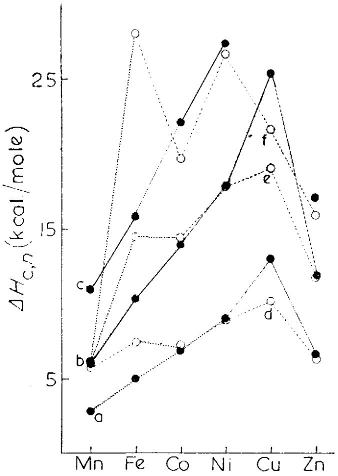

FIGURE 4. Heats of reaction, $\Delta H_{C,n}$, of transition metals with ethylenediamine (——●——), (*a*) $n = 1$; (*b*) $n = 2$; (*c*) $n = 3$; and with bipyridyl (- - -○- - -), (*d*) $n = 1$; (*e*) $n = 2$; (*f*) $n = 3$

It can be seen from Figure 4 that the values of the heat of formation, $\Delta H_{C,n}$, for mono-, bis-, and tris-complexes of ethylenediamine are very similar to those of the corresponding complexes of bipyridyl for cobalt, nickel, and zinc. The most obvious difference is the much larger heat of formation of the trisbipyridyliron(II) complex. But magnetic susceptibility measurements have shown that this complex is diamagnetic,[37] whereas the corresponding ethylenediamine complex is paramagnetic, as also is the hydrated ferrous ion. Hence, the ground state of the metal is changed when $Fe(bipy)_3^{2+}$ is formed from $Fe(H_2O)_6^{2+}$ and this would account for the larger enthalpy change. It should be noted that the value we have used in Figure 4 for $\Delta H_{C,2}$ for $Fe(bipy)_2^{2+}$ is quoted by the authors of ref. 7 as a very approximate upper limit and there is therefore no evidence that the heat of formation of $Fe(bipy)_2^{2+}$ is noticeably greater than that of $Fe(en)_2^{2+}$. Both $Fe(bipy)_2^{2+}$ and $Fe(en)_2^{2+}$ would be expected to be spin-free and therefore to have fairly similar heats of formation.

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[35] I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 1406.

[36] M. Ciampolini, P. Paoletti, and L. Sacconi, *J.*, 1960, 4552.

[37] F. H. Burstall and R. S. Nyholm, *J.*, 1952, 3570.

The stabilities of the copper complexes differ notably for the two ligands. The heats $\Delta H_{C,1}$ and $\Delta H_{C,2}$ are larger for ethylenediamine than for bipyridyl. Also, the third molecule of ethylenediamine is held quite weakly [35] and the heat of addition of the third molecule of ligand approaches zero. Both the heats and stability constants indicate that the third bipyridyl ligand attaches itself to copper(II) much more easily than does the third ethylenediamine ligand. These facts support Jørgensen's suggestion [38] that the bis-complex of copper with bipyridyl has the two water molecules *cis* to one another, whereas the bis-ethylenediamine complex ion $Cu\ (en)_2(H_2O)_2{}^{2+}$ is an elongated octahedron, the water molecules being in the *trans*-position with respect to the four equidistant coplanar nitrogen atoms. The high heat of formation of the bisethylenediamine complex is possibly due to the extra stabilisation arising from the Jahn–Teller distortion. If the bisbipyridyl complex of copper were the *trans*-isomer, a rearrangement would be necessary in order for the third bipyridyl ligand to become attached. Jørgensen [39] also points out that the high intensity of the absorption spectrum of $Cu(bipy)_2(H_2O)_2{}^{2+}$ supports the contention that it has mainly the *cis*-configuration.

Although the stability constants of bipyridyl and ethylenediamine complexes of manganese(II) are very similar, the heats of formation of bipyridyl and ethylenediamine complexes of manganese appear to differ widely, which is unexpected. It should be noted, however, that for the bipyridyl–manganese(II) system the stability constant, β_3, was obtained by extrapolation of the formation curve (the distribution method allowed experimental determinations only up to $\bar{n} = 1{\cdot}8$). Also, the value of the enthalpy change, assumed to be that arising from the formation of the tris-complex, was based on the fact that in a reaction where the ratio of ligand to metal was 50 : 1 the heat evolved was exactly the same as when the ratio was 100 : 1.

The only examples of negative entropy change were the trisbipyridyliron(II) complex and the monobipyridylmanganese(II) complex.

A comparison of the heats of formation of the trisbipyridyl complexes in the presence and absence of 1M-potassium nitrate did not show a constant difference independent of the metal, but in most cases ΔH_3 is about 0·5 kcal./mole higher for reactions in 1M-potassium nitrate.

Reactions of metal sulphates with bipyridyl in water, compared with 50% aqueous ethanol, showed for cobalt, nickel, and zinc an increase of 2 kcal./mole in the ethanolic solution, for copper an increase of 1 kcal./mole in ethanolic solution, but with manganese and iron a slight decrease in ethanol.

No general trend could be detected in the heats of formation of the trisbipyridyl complexes when different anions were associated with the metals. However, the heat of the reaction of ferrous sulphate with bipyridyl was 3 kcal./mole lower than that of the corresponding reaction with ferrous nitrate or ferrous perchlorate. It was also observed that the heat of reaction of copper(II) with bipyridyl was remarkably independent of the anion.

The results of Anderegg,[16] who measured the step-wise heats at 20° in 0·1M-sodium nitrate, are, except for the case of manganese, higher than ours, the discrepancy being largest for iron(II) (3·3 kcal./mole) and smallest for nickel (1·5 kcal./mole). This may possibly be due to the temperature difference of 10°.

Atkinson and Bauman [14] studied four metal–bipyridyl systems in which, according to their published figures, the maximum value of $\bar{n}$ reached was for Mn, 1·64; Ni, 1·44; Cu, 1·05, and Zn, 1·85. They assumed that, since the graph of ΔH_C versus $\bar{n}$ was linear for these low values of $\bar{n}$, it would continue to be so for values of $\bar{n}$ up to 3. This we found to be so for nickel, but our more detailed investigation showed that it is not true for manganese, cobalt, copper, and zinc. Both Anderegg [16] and we agree that the ΔH_C's for the successive steps are not equal in the case of cobalt(II), copper(II), and zinc(II). Also Anderegg's values for the three steps in the case of nickel(II) are approximately equal.

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[38] J. Bjerrum and C. K. Jørgensen, *Rec. Trav. chim.*, 1956, **75**, 658.

[39] C. K. Jørgensen. *Acta Chem. Scand.*, 1955, **9**, 1366.

Hence, we ought only, except for the case of nickel, to compare the values of the heats of formation of the monobipyridyl complexes obtained by Atkinson and Bauman [14] with ours and with Anderegg's. If temperature were the over-riding factor, the results for $\Delta H_{C,1}$ of Atkinson and Bauman, who worked at 25°, should lie between Anderegg's at 20° and ours at 30·3°. They do not for any of the four metals. They are all lower than ours, the value for copper(II) markedly so.

The other difference is that whereas Anderegg and we used metal nitrates and nitrate as background electrolyte, Atkinson and Bauman used metal perchlorate and perchlorate as background electrolyte. Our experiments using perchlorates (but not in a high-ionic-strength background) did in fact give a lower result for nickel(II) perchlorate than for nickel(II) nitrate under otherwise similar conditions. However, for the other metals the overall heats were almost the same for perchlorates as for nitrates.

We agree with Anderegg [16] on the relative magnitudes of the step-wise heats for Co(II) and Zn(II) but not for Cu(II). Anderegg finds the ratio of the first step to the second larger than we do; he also finds the third step-wise heat larger than the second, whereas we find it to be much smaller.

Our results for the ferrous sulphate–bipyridyl system are in good agreement with those obtained by Baxendale and George [7] from the variation of the stability constant, β_3, with temperature. They quote $24 \cdot 3 \pm 1 \cdot 3$ kcal./mole for $Fe(bipy)_3^{2+}$ at 25° and $I = 0 \cdot 025$. We obtained $24 \cdot 9 \pm 0 \cdot 3$ at 30·3° and $I =$ 1M-KNO_3.

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DEPARTMENT OF INORGANIC CHEMISTRY,
THE UNIVERSITY, BRISTOL 8.

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