RECEIVED BY DTIE JUN 18 1970
(15 May 1970)

C00-1782-3

A Calorimetric Study of Prussian Blue and Turnbull's Blue Formation^{1a}

By Reed M. Izatt^{1b}, Gerald D. Watt^{1c,d}, Calvin H. Bartholomew,
and James J. Christensen^{1b}.

MASTER

-
- (1) (a) Supported by U. S. Atomic Energy Commission Contract AT-(04-3)-299.
(b) To whom inquiries should be directed.
(c) Supported by a Public Health Service predoctoral fellowship (No. GM20, 545) from the Division of Research Grants, Public Health Service.
(d) Taken in part from the Ph.D. dissertation of Gerald D. Watt, *cf.* *Dissertation Abstr.*, 27, 1406-B (1966), Brigham Young University, Provo, Utah, June 1966.
-

Contribution from the Departments of Chemistry and Chemical Engineering and No. 5 from the Center for Thermochemical Studies, Brigham Young University, Provo, Utah 84601.

ABSTRACT

Values of ΔH° valid at zero ionic strength and 25° have been determined calorimetrically for the formation of "soluble" Prussian blue and Turnbull's blue from their constituent ions in dilute aqueous solution. The calorimetric data are shown to be consistent with literature data for the $\text{Fe}^{3+} - \text{Fe}(\text{CN})_6^{4-}$ redox reaction. The results are discussed in terms of the energy relationships for two proposed mechanisms of complex formation.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:
A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.
As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

leg

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTRODUCTION

The "soluble" forms,^{2,3} of Prussian blue and Turnbull's blue have been

- (2) "Mellor's Modern Inorganic Chemistry," G. D. Parkes, editor, John Wiley and Sons, Inc., New York, New York., Revised Edition, 1961, p. 927.
- (3) There appear to be two forms of Prussian and Turnbull's blue. One form "dissolves" in water giving a deeply colored blue "solution." This form is referred to as the "soluble" form and results when an equivalent of Fe^{2+} is added to $\text{Fe}(\text{CN})_6^{3-}$ or of Fe^{3+} to $\text{Fe}(\text{CN})_6^{4-}$. The "insoluble" form results when nonstoichiometric quantities of the above salts are mixed.² This paper deals primarily with the "soluble" form of Prussian and Turnbull's blue which is represented as $\text{KFeFe}(\text{CN})_6$.

known for many years and present interesting examples of the intense colors exhibited by species containing the same element in different oxidation states. For many years Prussian blue and Turnbull's blue were thought to be different, primarily because of the different methods by which they are formed as shown by reactions (1) and (2).

Keggin and Miles⁴ found the structures of the crystalline forms of Prussian

- (4) O. F. Keggin and F. D. Miles, Nature, 137, 577 (1936).

blue and Turnbull's blue to be identical, and to consist of one group of iron atoms surrounded by an octahedral arrangement of carbon atoms while another group of iron atoms is surrounded by an octahedral arrangement of nitrogen atoms. A theoretical

treatment⁵ of the electronic structure of Prussian blue based on ligand field theory

(5) M. B. Robin, Inorg. Chem., 1, 337 (1962).

considerations is consistent with the compound having the formula $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$. Mossbauer spectra⁶ of solid Prussian blue and Turnbull's blue indicate they are

(6) E. Fluck, "Advances in Inorganic Chemistry and Radio-chemistry," ed. by H. J. Emeleus and A. G. Sharpe, Academic Press, Vol. 6, 1964.

identical and these spectral data are in complete agreement with their formulation as a ferric ferrocyanide species. The Mossbauer spectra⁶ further indicate that very weak ionic bonding exists between the nitrogen end of the bonded cyanide ion and the ferric ion. A more complete discussion of the evidence for the identity and structure of solid Prussian blue and Turnbull's blue has recently appeared.⁷

(7) L. D. Hansen, W. M. Litchman and G. H. Daub, J. Chem. Ed., 46, 46 (1969).

A search of the literature reveals that no thermodynamic data have been reported for the formation of soluble Prussian blue and Turnbull's blue. Such data would be useful in understanding the energy relationships involved in such formation. In this paper are presented ΔH° values for the formation of the soluble forms of Prussian blue and Turnbull's blue from their respective ions.

EXPERIMENTAL

Materials. - Reagent grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Baker and Adamson), $\text{K}_4\text{Fe}(\text{CN})_6$ (Mallinckrodt), $\text{K}_3\text{Fe}(\text{CN})_6$ (Mallinckrodt), and standard iron wire (Baker and Adamson) were used in the preparation of solutions for this study. A $\text{Fe}(\text{ClO}_4)_3$ solution was prepared by dissolving a weighed amount of standard iron wire in a known volume of hot concentrated HClO_4 and diluting with an appropriate volume of water.

All solution preparations and manipulations were carried out under a nitrogen atmosphere to minimize oxidation of air sensitive compounds.

Procedure. - The calorimeter and supporting equipment have been described.⁸

-
- (8) J. D. Hale, R. M. Izatt, and J. J. Christensen, J. Phys. Chem., 67, 2605 (1963).
-

The calorimetric procedure consisted of adding 10 ml portions of 0.1 M potassium ferrocyanide and potassium ferricyanide solutions to 200 ml of 10^{-3} M ferric and ferrous solutions, respectively. The time interval from when the solutions were mixed to when the calorimetric measurement was finished was always less than 5 minutes. The reagents were mixed in stoichiometric amounts in order to avoid formation of any insoluble Prussian or Turnbull's blue.² Corrections were made for the dilution of potassium ferricyanide and potassium ferrocyanide using the heat of dilution data reported for these compounds by Lange and Miederer.⁹ In the 10^{-3} M

-
- (9) E. Lange and W. Miederer, Zeit. Elektrochem., 60, 34 (1956).
-

ferric ion solutions some hydrolysis of the ferric ion had occurred. A thermal correction for this hydrolysis was made as follows. A 10 ml portion of 2 M HClO_4 was added to the ferric ion solution and the total heat of interaction was measured. The difference between this measured heat and the heat of dilution of the HClO_4 ¹⁰ was taken to be the correction for the ferric ion hydrolysis. This

-
- (10) C. E. Vanderzee and J. A. Swanson, J. Phys. Chem., 67, 285 (1963).
-

correction was about -2 calories.

The time required to reach thermal equilibrium after reagents were mixed was approximately 2 to 3 minutes. The intense blue color of both Prussian and Turnbull's blue was observed to form instantly after mixing. Spectrophotometric

measurements at 680 mμ showed that a reasonably constant absorbance value was reached within two to three minutes after mixing. Although kinetic parameters have not been reported for the redox reaction,

one would expect the second order reverse rate constant to be of the order of magnitude of the forward rate constants reported for the Fe^{2+} - Fe^{3+} and $\text{Fe}(\text{CN})_6^{3-}$ - $\text{Fe}(\text{CN})_6^{4-}$ redox reactions of $3.2 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ ¹¹ and $1 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$,¹²

(11) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", New York (1968) p. 475.

(12) A. Loewenstein and G. Ron, Inorg. Chem., 6, 1604 (1967).

respectively. In fact, this value could be somewhat larger since one expects that a reaction between unlike ions would occur more rapidly than that between like ions.¹³ Furthermore, since the reported¹⁴ equilibrium constant for reaction (3)

(13) P. George and D. H. Irvine, J. Chem. Soc., 587 (1954).

(14) G. D. Watt, J. J. Christensen, and R. M. Izatt, Inorg. Chem., 4, 220 (1965).

is very large (1.82×10^8), the forward rate constant will be extremely large ($k_{\text{forward}} > 10^{11}$). For these reasons it is concluded that under the conditions of the experiment chemical equilibrium was attained well within the 2-3 minutes required to reach thermal equilibrium.

RESULTS

The calorimetric data for the reactions represented in (1) and (2) are given in Table I.

TABLE I
Calorimetric Data for Reactions (1) and (2) at 25°C.

$[\text{Fe}_T] \times 10^2$	Q_{Total}^a	$\Delta H(\text{kcal/mole})^b$
Reaction (1): $\text{Fe}^{2+} + \text{Fe}(\text{CN})_6^{3-} = \text{Turnbull's blue}$		
4.762	-17.000	-16.675
	-16.920	-16.595
	-17.045	-16.720
	-17.086	-16.761
	-17.093	-16.768
	-17.093	-16.768
		-16.715 ± 0.069
3.571	-12.731	-16.600
	-12.703	-16.563
	-12.699	-16.557
	-12.842	-16.748
	-12.794	-16.684
		-16.630 ± 0.083
2.381	- 8.349	-16.288
	- 8.334	-16.258
	- 8.349	-16.288
	- 8.350	-16.288
	- 8.354	-16.298
		-16.284 ± 0.073
1.191	- 4.091	-15.933
	- 4.066	-15.839
	- 4.103	-15.981

$[\text{Fe}_T] \times 10^2$	Q_{Total}^a	$\Delta H \text{ (kcal/möle)}^b$
	-3.975	$\frac{-15.468}{-15.805 \pm 0.156}$
Reaction (2): $\text{Fe}^{3+} + \text{Fe}(\text{CN})_6^{4-} = \text{Prussian blue}$		
9.532	-3.456	0.087
	-3.492	0.069
	-3.445	$\frac{0.091}{0.083 \pm 0.017}$
4.762	-2.945	0.283
	-2.971	0.256
	-2.968	$\frac{0.259}{0.266 \pm 0.017}$
2.381	-1.974	0.504
	-1.962	0.528
	-1.955	$\frac{0.543}{0.525 \pm 0.020}$

^aQ correction (cal), and mmoles of product, respectively, for each reaction at each $[\text{Fe}_T] \times 10^2$ are (1) $[\text{Fe}_T] = 4.762, -0.325, 1.000$; $[\text{Fe}_T] = 3.571, -0.281, 0.7500$; $[\text{Fe}_T] = 2.381, -0.213, 0.4995$; $[\text{Fe}_T] = 1.191, -0.111, 0.2498$; (2) $[\text{Fe}_T] = 9.532, -3.626, 1.945$; $[\text{Fe}_T] = 4.762, -3.220, 0.9722$; $[\text{Fe}_T] = 2.381, -2.219, 0.4864$. The Q correction term in each case is subtracted from Q_{Total} . The Q correction for reaction (2) includes a correction term for the slight hydrolysis of the Fe(III) solutions. ^bUncertainties are indicated as the standard deviation among runs.

Values for ΔH° were calculated from the data in Table I by extrapolating a plot of ΔH vs. total iron concentration, $[\text{Fe}_T]$, to $[\text{Fe}_T] = 0$. It was necessary to make the extrapolation against $[\text{Fe}_T]$ rather than ionic strength because the

uncertain nature of the "soluble" iron cyanide species made the calculation of the ionic strength impossible. The ΔH° values calculated in this manner for reactions (1) and (2) are -15.15 ± 0.35 and 0.72 ± 0.18 kcal/mole of Fe^{2+} and Fe^{3+} , respectively, where the uncertainties are estimated from the plots of ΔH° vs. Fe_T .

DISCUSSION

The difference between the reactants in reactions (1) and (2) is given by equation (3). The consistency of the ΔH° values reported for reactions (1) and (2) can now be checked by comparing their difference with the ΔH° value for reaction (3) since $\Delta H_2^\circ - \Delta H_1^\circ = \Delta H_3^\circ$. The agreement between the ΔH_3° value calculated from reactions (1) and (2), 15.87 ± 0.35 kcal/mole, and that reported earlier,¹⁴ 15.63 kcal/mole, is good.

The ΔH° values alone for reactions (1), (2) and (3) do not provide structural or mechanistic information regarding Prussian and Turnbull's blue. However, when viewed in light of spectral results, these values lead to interesting energy relationships. For instance, the earlier Mossbauer results⁶ and the observation¹⁵ of reasonably

(15) Y. Wu, Master Thesis, Brigham Young University, 1965 and unpublished results in this laboratory.

constant values for the extinction coefficient of Turnbull's blue over a range of concentrations suggest that Turnbull's blue and Prussian blue must be identical species in solution. Assuming this to be true, the ΔH values for reactions (1), (2) and (3) are consistent with the mechanism proposed by Fluck⁶ in which Prussian blue reacts by equation (2) and Turnbull's blue by equations (3) and (2) to form $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6^-$ in each case. Energetically this is reasonable because ΔH_3° is very small indicating that the energies of the reactants and products lie close together, *i.e.*, $\text{Fe}^{3+} + \text{Fe}(\text{CN})_6^{4-}$ are close in energy to $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6^-$. In the formation of Turnbull's blue the reactants Fe^{2+} and $\text{Fe}(\text{CN})_6^{3-}$ must be lowered about 15 kcal/mole in energy in order to form the blue colored complex by way of reaction (2). Certainly one mechanism is

not unique. It is possible to consider still another viewpoint consistent with a large negative enthalpy for reaction (1) and almost zero enthalpy for reaction (2).

In the crystal of $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ the two different oxidation states show preferential association⁵ for the carbon ends (Fe^{II}) and nitrogen ends (Fe^{III}), respectively, of the cyanide ligands. Assuming that this behavior can be extended to the species in solution, the formation of Turnbull's blue but not Prussian blue would cause a charge transfer transition (-42.03 kcal./mole of electrons)⁵ from Fe^{2+} to $\text{Fe}(\text{CN})_6^{3-}$, *i.e.*, $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^- \rightarrow \text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$. The effect of this charge transfer transition should be seen in the ΔH° value for reaction (1), but not in that for reaction (2). The larger ΔH° value for reaction (1) compared to that for reaction (2) is consistent with this explanation; however, the difference between the two ΔH° values (15.9 kcal./mole) is considerably less than the 42.0 kcal./mole expected from the charge transfer transition. Nevertheless, this viewpoint is not unreasonable since other energy terms besides the charge transfer transition are undoubtedly important in determining the magnitude of the measured ΔH° value.

Shriver, *et al.*,¹⁶ found that the ligand field strength of the cyanide ion

(16) D. F. Shriver, S. A. Shriver, and S. E. Anderson, Inorganic Chemistry,
4, 725 (1965).

when bonded through nitrogen was comparable to that of H_2O . This finding is generally supported by the data presented here. In the reaction of ferric ion with ferrocyanide ion the six water molecules surrounding the ferric ion are replaced by the nitrogen ends of six cyanide ions. Since the ΔH° value for reaction (2) is very close to zero (0.72 kcal./mole) the nitrogen ends of the bonded cyanide ions appear to have essentially the same effect as the water molecules they have replaced.

(15 May 1970)

A Calorimetric Study of Prussian Blue and Turnbull's Blue Formation^{1a}

By Reed M. Izatt^{1b}, Gerald D. Watt^{1c,d}, Calvin H. Bartholomew,
and James J. Christensen^{1b}.

-
- (1) (a) Supported by U. S. Atomic Energy Commission Contract AT-(04-3)-299.
(b) To whom inquiries should be directed.
(c) Supported by a Public Health Service predoctoral fellowship (No. GM20, 545) from the Division of Research Grants, Public Health Service.
(d) Taken in part from the Ph.D. dissertation of Gerald D. Watt, *cf.* *Dissertation Abstr.*, 27, 1406-B (1966), Brigham Young University, Provo, Utah, June 1966.
-

Contribution from the Departments of Chemistry and Chemical Engineering and No. 5 from the Center for Thermochemical Studies, Brigham Young University, Provo, Utah 84601.

ABSTRACT

Values of ΔH° valid at zero ionic strength and 25° have been determined calorimetrically for the formation of "soluble" Prussian blue and Turnbull's blue from their constituent ions in dilute aqueous solution. The calorimetric data are shown to be consistent with literature data for the $\text{Fe}^{3+} - \text{Fe}(\text{CN})_6^{4-}$ redox reaction. The results are discussed in terms of the energy relationships for two proposed mechanisms of complex formation.

INTRODUCTION

The "soluble" forms,^{2,3} of Prussian blue and Turnbull's blue have been

- (2) "Mellor's Modern Inorganic Chemistry," G. D. Parkes, editor, John Wiley and Sons, Inc., New York, New York., Revised Edition, 1961, p. 927.
- (3) There appear to be two forms of Prussian and Turnbull's blue. One form "dissolves" in water giving a deeply colored blue "solution." This form is referred to as the "soluble" form and results when an equivalent of Fe^{2+} is added to $\text{Fe}(\text{CN})_6^{3-}$ or of Fe^{3+} to $\text{Fe}(\text{CN})_6^{4-}$. The "insoluble" form results when nonstoichiometric quantities of the above salts are mixed.² This paper deals primarily with the "soluble" form of Prussian and Turnbull's blue which is represented as $\text{KFeFe}(\text{CN})_6$.

known for many years and present interesting examples of the intense colors exhibited by species containing the same element in different oxidation states. For many years Prussian blue and Turnbull's blue were thought to be different, primarily because of the different methods by which they are formed as shown by reactions (1) and (2).

Keggin and Miles⁴ found the structures of the crystalline forms of Prussian

- (4) O. F. Keggin and F. D. Miles, Nature, **137**, 577 (1936).

blue and Turnbull's blue to be identical, and to consist of one group of iron atoms surrounded by an octahedral arrangement of carbon atoms while another group of iron atoms is surrounded by an octahedral arrangement of nitrogen atoms. A theoretical

treatment⁵ of the electronic structure of Prussian blue based on ligand field theory

(5) M. B. Robin, Inorg. Chem., 1, 337 (1962).

considerations is consistent with the compound having the formula $KFe^{III}[Fe^{II}(CN)_6]$. Mossbauer spectra⁶ of solid Prussian blue and Turnbull's blue indicate they are

(6) E. Fluck, "Advances in Inorganic Chemistry and Radio-chemistry," ed. by H. J. Emeleus and A. G. Sharpe, Academic Press, Vol. 6, 1964.

identical and these spectral data are in complete agreement with their formulation as a ferric ferrocyanide species. The Mossbauer spectra⁶ further indicate that very weak ionic bonding exists between the nitrogen end of the bonded cyanide ion and the ferric ion. A more complete discussion of the evidence for the identity and structure of solid Prussian blue and Turnbull's blue has recently appeared.⁷

(7) L. D. Hansen, W. M. Litchman and G. H. Daub, J. Chem. Ed., 46, 46 (1969).

A search of the literature reveals that no thermodynamic data have been reported for the formation of soluble Prussian blue and Turnbull's blue. Such data would be useful in understanding the energy relationships involved in such formation. In this paper are presented ΔH° values for the formation of the soluble forms of Prussian blue and Turnbull's blue from their respective ions.

EXPERIMENTAL

Materials. - Reagent grade $FeSO_4 \cdot 7H_2O$ (Baker and Adamson), $K_4Fe(CN)_6$ (Mallinckrodt), $K_3Fe(CN)_6$ (Mallinckrodt), and standard iron wire (Baker and Adamson) were used in the preparation of solutions for this study. A $Fe(ClO_4)_3$ solution was prepared by dissolving a weighed amount of standard iron wire in a known volume of hot concentrated $HClO_4$ and diluting with an appropriate volume of water.

All solution preparations and manipulations were carried out under a nitrogen atmosphere to minimize oxidation of air sensitive compounds.

Procedure. - The calorimeter and supporting equipment have been described.⁸

-
- (8) J. D. Hale, R. M. Izatt, and J. J. Christensen, J. Phys. Chem., 67, 2605 (1963).
-

The calorimetric procedure consisted of adding 10 ml portions of 0.1 M potassium ferrocyanide and potassium ferricyanide solutions to 200 ml of 10^{-3} M ferric and ferrous solutions, respectively. The time interval from when the solutions were mixed to when the calorimetric measurement was finished was always less than 5 minutes. The reagents were mixed in stoichiometric amounts in order to avoid formation of any insoluble Prussian or Turnbull's blue.² Corrections were made for the dilution of potassium ferricyanide and potassium ferrocyanide using the heat of dilution data reported for these compounds by Lange and Miederer.⁹ In the 10^{-3} M

-
- (9) E. Lange and W. Miederer, Zeit. Elektrochem., 60, 34 (1956).
-

ferric ion solutions some hydrolysis of the ferric ion had occurred. A thermal correction for this hydrolysis was made as follows. A 10 ml portion of 2 M HClO_4 was added to the ferric ion solution and the total heat of interaction was measured. The difference between this measured heat and the heat of dilution of the HClO_4 ¹⁰ was taken to be the correction for the ferric ion hydrolysis. This

-
- (10) C. E. Vanderzee and J. A. Swanson, J. Phys. Chem., 67, 285 (1963).
-

correction was about -2 calories.

The time required to reach thermal equilibrium after reagents were mixed was approximately 2 to 3 minutes. The intense blue color of both Prussian and Turnbull's blue was observed to form instantly after mixing. Spectrophotometric

measurements at 680 mμ showed that a reasonably constant absorbance value was reached within two to three minutes after mixing. Although kinetic parameters have not been reported for the redox reaction,

one would expect the second order reverse rate constant to be of the order of magnitude of the forward rate constants reported for the Fe^{2+} - Fe^{3+} and $\text{Fe}(\text{CN})_6^{3-}$ - $\text{Fe}(\text{CN})_6^{4-}$ redox reactions of $3.2 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ ¹¹ and $1 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$,¹²

(11) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", New York (1968) p. 475.

(12) A. Loewenstein and G. Ron, Inorg. Chem., 6, 1604 (1967).

respectively. In fact, this value could be somewhat larger since one expects that a reaction between unlike ions would occur more rapidly than that between like ions.¹³ Furthermore, since the reported¹⁴ equilibrium constant for reaction (3)

(13) P. George and D. H. Irvine, J. Chem. Soc., 587 (1954).

(14) G. D. Watt, J. J. Christensen, and R. M. Izatt, Inorg. Chem., 4, 220 (1965).

is very large (1.82×10^8), the forward rate constant will be extremely large ($k_{\text{forward}} > 10^{11}$). For these reasons it is concluded that under the conditions of the experiment chemical equilibrium was attained well within the 2-3 minutes required to reach thermal equilibrium.

RESULTS

The calorimetric data for the reactions represented in (1) and (2) are given in Table I.

TABLE I
Calorimetric Data for Reactions (1) and (2) at 25°C.

$[\text{Fe}_T] \times 10^2$	Q_{Total}^a	$\Delta H(\text{kcal/mole})^b$
Reaction (1): $\text{Fe}^{2+} + \text{Fe}(\text{CN})_6^{3-} = \text{Turnbull's blue}$		
4.762	-17.000	-16.675
	-16.920	-16.595
	-17.045	-16.720
	-17.086	-16.761
	-17.093	-16.768
	-17.093	-16.768
		$\frac{-16.768}{-16.715 \pm 0.069}$
3.571	-12.731	-16.600
	-12.703	-16.563
	-12.699	-16.557
	-12.842	-16.748
	-12.794	-16.684
		$\frac{-16.684}{-16.630 \pm 0.083}$
2.381	- 8.349	-16.288
	- 8.334	-16.258
	- 8.349	-16.288
	- 8.350	-16.288
	- 8.354	-16.298
		$\frac{-16.298}{-16.284 \pm 0.073}$
1.191	- 4.091	-15.933
	- 4.066	-15.839
	- 4.103	-15.981

$[\text{Fe}_T] \times 10^2$	Q_{Total}^a	$\Delta H \text{ (kcal/mole)}^b$
	-3.975	$\frac{-15.468}{-15.805 \pm 0.156}$
Reaction (2): $\text{Fe}^{3+} + \text{Fe}(\text{CN})_6^{4-} = \text{Prussian blue}$		
9.532	-3.456	0.087
	-3.492	0.069
	-3.445	$\frac{0.091}{0.083 \pm 0.017}$
4.762	-2.945	0.283
	-2.971	0.256
	-2.968	$\frac{0.259}{0.266 \pm 0.017}$
2.381	-1.974	0.504
	-1.962	0.528
	-1.955	$\frac{0.543}{0.525 \pm 0.020}$

^aQ correction (cal), and mmoles of product, respectively, for each reaction at each $[\text{Fe}_T] \times 10^2$ are (1) $[\text{Fe}_T] = 4.762, -0.325, 1.000$; $[\text{Fe}_T] = 3.571, -0.281, 0.7500$; $[\text{Fe}_T] = 2.381, -0.213, 0.4995$; $[\text{Fe}_T] = 1.191, -0.111, 0.2498$; (2) $[\text{Fe}_T] = 9.532, -3.626, 1.945$; $[\text{Fe}_T] = 4.762, -3.220, 0.9722$; $[\text{Fe}_T] = 2.381, -2.219, 0.4864$. The Q correction term in each case is subtracted from Q_{Total} . The Q correction for reaction (2) includes a correction term for the slight hydrolysis of the Fe(III) solutions. ^bUncertainties are indicated as the standard deviation among runs.

Values for ΔH° were calculated from the data in Table I by extrapolating a plot of ΔH vs. total iron concentration, $[\text{Fe}_T]$, to $[\text{Fe}_T] = 0$. It was necessary to make the extrapolation against $[\text{Fe}_T]$ rather than ionic strength because the

uncertain nature of the "soluble" iron cyanide species made the calculation of the ionic strength impossible. The ΔH° values calculated in this manner for reactions (1) and (2) are -15.15 ± 0.35 and 0.72 ± 0.18 kcal/mole of Fe^{2+} and Fe^{3+} , respectively, where the uncertainties are estimated from the plots of ΔH° vs. Fe_T .

DISCUSSION

The difference between the reactants in reactions (1) and (2) is given by equation (3). The consistency of the ΔH° values reported for reactions (1) and (2) can now be checked by comparing their difference with the ΔH° value for reaction (3) since $\Delta H_2^\circ - \Delta H_1^\circ = \Delta H_3^\circ$. The agreement between the ΔH_3° value calculated from reactions (1) and (2), 15.87 ± 0.35 kcal/mole, and that reported earlier,¹⁴ 15.63 kcal/mole, is good.

The ΔH° values alone for reactions (1), (2) and (3) do not provide structural or mechanistic information regarding Prussian and Turnbull's blue. However, when viewed in light of spectral results, these values lead to interesting energy relationships. For instance, the earlier Mossbauer results⁶ and the observation¹⁵ of reasonably

(15) Y. Wu, Master Thesis, Brigham Young University, 1965 and unpublished results in this laboratory.

constant values for the extinction coefficient of Turnbull's blue over a range of concentrations suggest that Turnbull's blue and Prussian blue must be identical species in solution. Assuming this to be true, the ΔH values for reactions (1), (2) and (3) are consistent with the mechanism proposed by Fluck⁶ in which Prussian blue reacts by equation (2) and Turnbull's blue by equations (3) and (2) to form $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6^-$ in each case. Energetically this is reasonable because ΔH_3° is very small indicating that the energies of the reactants and products lie close together, *i.e.*, $\text{Fe}^{3+} + \text{Fe}(\text{CN})_6^{4-}$ are close in energy to $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6^-$. In the formation of Turnbull's blue the reactants Fe^{2+} and $\text{Fe}(\text{CN})_6^{3-}$ must be lowered about 15 kcal/mole in energy in order to form the blue colored complex by way of reaction (2). Certainly one mechanism is

not unique. It is possible to consider still another viewpoint consistent with a large negative enthalpy for reaction (1) and almost zero enthalpy for reaction (2).

In the crystal of $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ the two different oxidation states show preferential association⁵ for the carbon ends (Fe^{II}) and nitrogen ends (Fe^{III}), respectively, of the cyanide ligands. Assuming that this behavior can be extended to the species in solution, the formation of Turnbull's blue but not Prussian blue would cause a charge transfer transition (-42.03 kcal./mole of electrons)⁵ from Fe^{2+} to $\text{Fe}(\text{CN})_6^{3-}$, i.e., $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^- \rightarrow \text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$. The effect of this charge transfer transition should be seen in the ΔH° value for reaction (1), but not in that for reaction (2). The larger ΔH° value for reaction (1) compared to that for reaction (2) is consistent with this explanation; however, the difference between the two ΔH° values (15.9 kcal./mole) is considerably less than the 42.0 kcal./mole expected from the charge transfer transition. Nevertheless, this viewpoint is not unreasonable since other energy terms besides the charge transfer transition are undoubtedly important in determining the magnitude of the measured ΔH° value.

Shriver, *et al.*,¹⁶ found that the ligand field strength of the cyanide ion

(16) D. F. Shriver, S. A. Shriver, and S. E. Anderson, Inorganic Chemistry,
4, 725 (1965).

when bonded through nitrogen was comparable to that of H_2O . This finding is generally supported by the data presented here. In the reaction of ferric ion with ferrocyanide ion the six water molecules surrounding the ferric ion are replaced by the nitrogen ends of six cyanide ions. Since the ΔH° value for reaction (2) is very close to zero (0.72 kcal./mole) the nitrogen ends of the bonded cyanide ions appear to have essentially the same effect as the water molecules they have replaced.