Thermochimica Acta, 23 (1978) 321–327

THE ENTHALPIMETRIC DETERMINATION OF MIXTURES OF SULPHUR-CONTAINING ANIONS

L. S. BARK* AND A. E. NYA**
The Ramage Laboratories, University of Salford, Salford M5 4WT (England)
(Received 24 May 1977)

ABSTRACT

Using the concept of the additivity of partial molar heat pulses, a series of mixtures containing all or some of the following anions (S^{2-}, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$) and S have been determined by the use of selected but non-selective reactions. The accuracy at the mM level is within 1.5%.

INTRODUCTION

We have previously[1] proposed the concept of Partial Molar Temperature Pulses and indicated its use in the enthalpimetric determination of a series of halide mixtures. In any particular enthalpimetric titration system, having a constant volume and thermal capacity, we have indicated that for any reaction involving a mixture of analytes, the total temperature pulse will be the sum of all the partial temperature pulses of the components of the mixture. The partial temperature pulse of any analyte is that which would be obtained, by the reaction between the particular reagent and analyte if that analyte component alone occupied the whole sample volume. Thus, the recorded heat pulse (P actual) is such that:

P actual $= \Sigma(aP_A + bP_B + cP_C \ldots iP_I + P_M)$ where $a, b, c \ldots i$

represent the number of moles of analytes A, B, C ... I, having partial molar temperature pulses of P_A, P_B, P_C ... P_I, respectively, and P_M is the temperature pulse representing the dilution of the reagent, i.e., is dependent upon the heat of mixing.

The partial temperature pulse for any component is equal to the number of moles of that component present in the sample volume *times* the partial molar temperature pulse for that analyte in that particular system.

The partial molar temperature pulse is determined by reacting known amounts of the particular analyte, with the reagent being used. The volumes of the sample, the

---

* To whom all correspondence should be addressed.
** On leave from The University of Benin, Benin City, Nigeria.

reagent, the general enthalpimetric system must be kept constant both for the calibration and for the assay.

The total number of reactions and hence of reagents, which need not be selective, but which must react with at least one component of the mixture, must be at least equal to the number of components to be determined. Since all the reactions may not have heats of reaction of the same order of magnitude, it may be necessary to adjust the sensitivity of the system in order to obtain a signal of an acceptable size. This may be done either by altering the sensitivity of the electrical bridge and/or that of the potentiometric recorder or it may be more practicable to dilute the sample so that the fixed volume of solution in the reaction vessel contains less analyte. Thus, we have the possibility of having signals obtained at different sensitivities and for different concentrations of the analyte for various reactions in the overall assay. In order to be able to expedite calculations, it is useful to use the term "System Heat Pulse", viz., the heat pulse which would be obtained in that particular titration system, using a sensitivity of a Full Scale Deflection (F.S.D.) for 1 mV when 1 mM of the analyte is contained in the fixed volume (V) of the sample.

For example, in the system used, 1 mM of sulphide ion in 20 ml of sample, when reacted with Ag^+ would give a deflection of 1000 mm, using 1 mV for an F.S.D. Since the total width of the scale is only 250 mm, in order to obtain a measureable signal, we may use a sensitivity of 5 mV for F.S.D. to obtain 200 mm deflection per 1 mM of sulphide in 20 ml of sample, or dilute the sample so that 20 ml contains only 0.25 mM in 20 ml and, using a sensitivity of 2 mV for F.S.D., we would obtain a reading of 125 mm.

Thus, to obtain a measurable deflection (heat pulse) on the apparatus provided, one may dilute the sample and/or alter the sensitivity of the recorder, and thence by simple calculation convert the experimental results from those obtained to the equivalent System Heat Pulse. e.g.: If the heat pulse obtained under the conditions defined for the System Heat Pulse is Δ_{SHP} then:

$\Delta_{expt}/\Delta_{SHP}$ = sensitivity (in mV) used for F.S.D. × dilution ratio of sample

EXPERIMENTAL

Titration system

The direct injection enthalpimetric titration systems has been previously described[2]. The working volume was 20 ml. The amount of reagent injected was constant and nominally 1 ml. The recorder used to measure the heat pulse was capable of being adjusted to record 0.25 mV, 0.5 mV, 1.0 mV, 2.0, 5.0 mV for an F.S.D. of 250 mm.

Reagents

For calibration purposes, series of single salt solutions were prepared, containing 0 to 1 mM of the sulphur anion per 20 ml of solution. The following materials were used: sulphur, reagent grade sodium sulphide, A.R. grade sodium thiosulphate,

TABLE 1

SINGLE SYSTEM

Titration of sodium sulphite with iodine solution (2 mV for full scale deflection). Calculated system molar heat pulse = 1000 (i.e., I_2/SO_3^{2-} = 1000).

No. of mM of analyte/20 ml	*Temp. pulse*				*Average adjusted for dilution*
	1	*2*	*3*	*4*	
0.0	−13	−13	−13	−13	0
0.2	24	23	24	24	37
0.4	60	60	60	60	73
0.6	102	102	102	102	115
0.8	140	140	140	140	153
1.0	180	180	179	180	193

TABLE 2

BINARY MIXTURES

Titration of sodium sulphide and sodium thiosulphate with (i) iodine (2mV F.S.D.) and (ii) silver (solution diluted 10 times; 0.5mV F.S.D.).

Amount mM/20ml added		*"Iodine pulse" (corrected for dilution)*		*"Silver pulse" (corrected for dilution)*		*Amount/20 ml*[a]	
Na_2S	*$Na_2S_2O_3$*					*Na_2S*	*$Na_2S_2O_3$*
0.1	0.1	82[b]	82.7[c]	121[b]	120[c]	0.097	1.006
0.2	0.8	105	105	120	120	0.198	0.805
0.4	0.6	163	161	140	140	0.409	0.59
0.6	0.4	216	216	160	160	0.599	0.402
0.8	0.2	273	272	180	180	0.801	0.201
1.0	0.1	233	332	210	210	1.0004	0.10

[a] Values calculated by conversion of all signals to system heat pulse for the analytes, and then solving of the appropriate simultaneous equations of Table 3.

[b] Actual value recorded, adjusted for dilution and sensitivity.

[c] Value calculated by addition of partial molar temperature pulses.

TABLE 3

BINARY SYSTEM/QUATERNARY SYSTEM

Titration of (a) Sodium thiosulphate + sodium sulphide; (b) sodium thiosulphate + sodium sulphide in the presence of sodium sulphite + sodium sulphate (which have zero heats of reaction in this system) with Cd^{2+} (2mV F.S.D.).

Amount of anion in 20 ml (mM)				*Pulse recorded*	
S^{2-}	*$S_2O_3^{2-}$*	*SO_4^{2-}*	*SO_3^{2-}*	*a*	*b*
0.1	1.0	4	4	−11.5	−11.5
0.2	0.8	5	5	15.5	15.5
0.4	0.6	5	5	64	64.5
0.6	0.4	5	5	111	111
0.8	0.2	5	5	157.5	157.5
1.0	0.1	4	4	200	200.5

(*a*) Pulse recorded on binary system, corrected for heat of dilution.

(*b*) Pulse recorded on quaternary system, corrected for heat of dilution.

TABLE 4

BINARY SYSTEM

Titration of sulphide and sulphite with Cd^{2+} solution (2mV) and Ag^{+} solution (0.5 mV) (solution diluted × 10).

Amount of analyte in 20 ml (in mM)

Added		*Calculated*	
Sulphide	*Sulphite*	*Sulphide*	*Sulphite*
0.10	1.00	0.10(0)	1.00
0.20	0.80	0.20(0)	0.79(9)
0.40	0.60	0.40(3)	0.58(8)
0.80	0.20	0.79(9)	0.20(1)
1.00	0.10	0.97	0.097

TABLE 5

BINARY SYSTEM

Titration of sulphite and thiosulphate with iodine (2mV FSD) and silver (0.5mV FSD) (solution diluted × 10).

Amount of analyte in 20 ml (in mM)

Added		*Calculated*	
Sulphite	*Thiosulphate*	*Sulphite*	*Thiosulphate*
0.10	1.00	0.09(9)	0.99(8)
0.20	0.80	0.19(7)	0.79(9)
0.40	0.60	0.39(3)	0.60(0)
0.60	0.40	0.59(5)	0.40(3)
0.80	0.20	0.79(2)	0.20(2)
1.00	0.10	1.00	0.10(0)

TABLE 6

TERNARY MIXTURES

Titration of mixtures of sulphide, thiosulphate and sulphite with cadmium solution; silver solution (solution diluted × 10); iodine solution.

Amount of analyte in 20 ml (in mM)

Added			*Calculated*		
SO_3^{2-}	S^{2-}	$S_2O_3^{2-}$	SO_3^{2-}	S^{2-}	$S_2O_3^{2-}$
0.10	0.10	0.10	0.098(7)	0.099(8)	0.10(4)
0.20	0.20	0.20	0.20(0)	0.20(0)	0.20(4)
0.40	0.40	0.40	0.399(6)	0.39(6)	0.40(1)
0.60	0.60	0.60	0.6(0)	0.60(0)	0.60(0)

TABLE 7

QUATERNARY MIXTURES

Titration of mixtures of sulphide, thiosulphate, sulphite and sulphate with barium solution; silver solution; cadmium solution; and iodine solution.

Amount of analyte in 20 ml (in mM)							
Added				*Calculated*			
S^{2-}	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}	S^{2-}	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}
0.10	0.10	0.10	0.10	0.09(9)	0.10(1)	0.10(1)	0.10(1)
0.20	0.20	0.20	0.20	0.19(9)	0.20(2)	0.20(0)	0.20(0)
0.40	0.40	0.40	0.40	0.39(9)	0.40(1)	0.38(9)	0.41(3)
0.60	0.60	0.60	0.60	0.61(0)	0.60(0)	0.59(8)	0.61(5)

9. Addition of sulphur no significant effects were noticed in any mixture.

TABLE 8

SYSTEM HEAT PULSE FOR ANALYTES (1mM in 20 ml; 1mV F.S.D.)

Analyte	*Reagent used for reaction*			
(1mM in 20 ml)	Ba^{2+}	Cd^{2+}	I_2	Ag^+
Sulphide	0	410	654	1000
Thiosulphate	0	0	100	500
Sulphite	50	−64	386	200
Sulphate	108	0	0	0
Sulphur	0	0	0	0

reagent grade sodium sulphite, and A.R. grade sodium sulphate. The solutions were standardised by conventional methods[3].

(1) *Cadmium solution.* 2.5 M Cd^{2+} (as $Cd(NO_3)_2$) was prepared and used as the reactant for one system.

(2) *Barium solution.* 2 M Ba^{2+} (as $BaBr_2$) was prepared from reagent grade material.

(3) *I_2 solution.* 2 M I_2 in KI solution.

(4) *Silver solution.* 0.25 M (as $AgNO_3$) prepared from reagent grade salt.

Titrations

For titrations with Cd^{2+}, I_2, Ba^{2+} the solutions contained 0 to 1.0 mM of analyte per 20 ml of sample. For titrations with Ag^+, the analyte samples were diluted ten times. For Cd^{2+}, I_2, Ba^{2+} titrations the sensitivity was adjusted to give F.S.D. for 2 mV; for Ag^+ a sensitivity of F.S.D. for 0.5 mV was used. Some binary, ternary, quaternary and quinary mixtures were synthesised, by suitable mixture of the analytes (sulphur anions and sulphur). The results are given in Tables 1–7.

Where the molar heat of reaction was zero for the analytes (sulphate, thiosulphate in their reaction with Cd^{2+}), a binary and a quaternary system are compared, in order to assess the effect of extra non-reacting components on the heat pulses of the analytes.

Each titration was done in triplicate. Sulphur (up to 3 mg) was added to selected systems.

RESULTS

A summary of the results on single compounds is given in Table 8.

Discussion of Results

Considering Table 2, for the titration of mixtures of sulphide and thiosulphate, in order to calculate the value of the pulses expected by addition of partial molar pulses, one assumes that there is no interaction of the sulphide and thiosulphate, and that any alteration in the ionic strengths of the sample ... causes no alteration in the thermal capacity of the system.

Thus, in order to calculate the composition of the mixture, the experimental signals are converted to the equivalent system heat pulses, and then the appropriate simultaneous equations are solved, viz., If the heat pulse for the iodine system is Δ_{I_2}, and the heat pulse for the silver ion system is Δ_{Ag^+}, i.e., heat pulse recorded, adjusted for dilution and sensitivity, then if x and y are the number of mM of thiosulphate and sulphide, respectively, in 20 ml of sample solution;

Heat pulse $= x \cdot$ system heat pulse for I_2/thiosulphate $+ y \cdot$ system heat pulse I_2/S^{2-}
(I_2 system)

Heat pulse $= x \cdot$ system heat pulse for Ag^+/thiosulphate $+ y \cdot$ system heat pulse Ag^+/S^{2-}
(Ag^+ system)

Thus, for say mixture (4) (0.60 mM of Na_2S + 0.40 mM of $Na_2S_2O_3$);

The heat pulse for the I_2 system is 216 mM, and the experimental heat pulse for the Ag^+ system is 160 mM.

Thus:

$$216 = 100x + 654y \tag{1}$$

$$160 = 500x + 1000y \tag{2}$$

Solving these equations gives $x = 0.599$ mM and $y = 0.402$ mM.

Similarly, for the quaternary system of sulphide, thiosulphate, sulphite, and sulphate, for any particular mixture there are four simultaneous equations valid. These relate respectively to the experimental heat pulses obtained by injection of samples of barium solution, silver ion solution, cadmium solution and iodine solution into 4 separate aliquots.

From a consideration of the results it appears that the accuracy of the method is generally better than 1.5%, over the range 0 to 1 mM of each analyte and over the range of 0 to 2.5 mM of total analyte. The method is rapid; for example in the quaternary system, the solving of the four equations requires approximately 10 steps, and these are easily programmed, so that for routine assays, only 4 numbers need to be fed into the programme.

The reactions chosen were selected on one main criterion: they were all rapid reactions, practically instantaneous. Although it is theoretically possible to use reactions for which the molar heats of reaction for the analytes are widely different, this will obviously reduce the accuracy of the method, since small errors in one may be of great significance additively. We have thus selected those reactions where the molar heats for the reacting species are of the same order. The heat of dilution of the reagent must also be fairly small, so that the signal obtained is not mainly due to dilution effects. Obviously the amount of dilution will vary, depending on the amount of reagent used in the analyte reaction, i.e., the greater the amount of reagent used the smaller is the effect due to dilution. We thus considered the heats of dilution of each reagent and have used that amount which would not give a variation of more than 1–2 units, over the range of analytes present. This error is systematic and by the use of a suitable iterative programme incorporating the variation in the amount of dilution, with the amounts of analytes present, the error may be eliminated. For our purposes, such sophistication was not required.

It would appear that the method should be able to be applied for any number of analytes in a sample. It will be necessary to have selected reactions, which give suitable heat changes, but it is obviously not necessary to have specific or selective reactions.

ACKNOWLEDGEMENT

One of us (AEN) thanks UNESCO for the provision of a Fellowship, during which this work was carried out.

REFERENCES

1 L. S. Bark and A. E. Nya, J. Therm. Anal., 12 (1977) 277.
2 L. S. Bark and J. K. Grime, *Analyst*, 97 (1972) 911.
3 A. I. Vogel, *Quantitative Inorganic Analysis*, Longman, Green, London.