Journal of Thermal Analysis, Vol. 12 (1977) 277—283

THE ENTHALPIMETRIC DETERMINATION OF MIXTURES CONTAINING PHOSPHATE, ARSENATE(V) AND ARSENATE(III) IONS

L. S. BARK and A. E. NYA*

The Ramage Laboratories, University of Salford, Salford M5 4WT, U.K.

(Received February 9, 1977)

A series of mixtures, each containing at least two of the ions phosphate, arsenate(V) and arsenate(III) have been determined enthalpimetrically using the concept of the additivity of partial molar heat pulses. The non-selective reactions used involved precipitation and redox reactions. The accuracy at the 1 *mM* level is within 1.5%, and the total time of a determination of a mixture of all three anions is less than 10 minutes after preparation of the sample solution, which is prepared for insoluble phosphates, by metathesis with sodium carbonate.

The principles of direct injection enthalpimetry are well established. Several workers [1—3] have applied enthalpimetric methods for the determination of mixtures of ions. In order that at any one time, only one component of the mixture reacts with the particular reagent used, the reactions have to be highly selective. This condition severely restricts the choice of reagent and results either in the need for preliminary separation of a complex mixture into simpler mixtures, or makes it virtually impossible to determine mixtures of chemically related species. We have previously proposed the use of non-selective reactions and the concept of Partial Molar Temperature Pulses [4] and have indicated the use of the concept in the enthalpimetric determination to a series of chemically similar species (halide ions) [5], and of a series of related anions, based on the same element in different oxidation states (sulphide, thiosulphate, sulphite and sulphate) [6]. The use has now been extended to mixtures containing anions of both types, e.g. phosphate, arsenate(V) and arsenate(III). The reaction systems selected involve oxidation-reduction and precipitation reactions, as well as reactions with different rates, since it was considered feasible to utilise the difference in reaction rates to achieve some analytical selectivity.

The reactions used for assay purposes were chosen on the basis of the following criteria: (a) the molar heats of reaction of the various analytes were either of the same order, or the molar heat of one reaction was practically zero; (b) the reactions were either practically instantaneous, or did not occur to any significant extent within 10 seconds of mixing the reactants.

---

* On leave from The University of Benin, Benin City, Nigeria

In order to measure a suitable heat pulse on the apparatus used, one may require to dilute the sample and/or alter the sensitivity of either or both of the bridge and the electrical recorder, and thence by simple calculation convert the experimental results to the equivalent system heat pulse [6], which is defined as "the heat pulse which would be obtained in that particular titration system, using a sensitivity such that a Full Scale Deflection (FSD) is obtained for 1 *m*Volt when 1 *m*Mole of the analyte is contained in the fixed volume (*V* ml) of the sample".

If the heat pulse (pen deflection) obtained experimentally is Δ_{expt}, and if the equivalent heat obtained under the conditions defined for the system heat pulse is ΔSHP then: The number of *m*Moles of analyte in *V* ml of prepared sample $= \frac{\Delta_{expt}}{\Delta SHP} \cdot$ number of mVolts required to give 1 FSD of the recorder under the experimental conditions.

To some extent the heat of dilution of the reagents imposes some restriction upon the choice of reaction. It has previously been found that if it is necessary to amplify the heat pulses, in order to give an analyte reaction pulse of a reasonable size (arbitrarily chosen as a pen deflection of not less than 75 mm), then this is not always possible if the heat of dilution is high either exothermically or endothermically, since the heat of dilution which is part of the system heat pulse, is also amplified.

Experimental

Apparatus

The enthalpimetric system has been previously described [7]. The working volume of the prepared sample was fixed at 20 ml and the amount of each reagent injected was constant and contained in a fixed volume (nominally 1 ml) of reagent solution. The recorder used to measure the heat pulse, manifested as an off-balance voltage from the Wheatstone bridge circuit, was capable of recording from 0.5 mV to 5 mV for a FSD of 250 mm pen deflection. (In practice the readings were generally taken using a sensitivity of 0.5 mV FSD.) The determinations were all done in a temperature controlled room at 25°.

Analyte solution and mixtures

Aqueous solutions of trisodium phosphate, disodium hydrogen arsenate(III) were prepared and standardized by conventional methods. From these stock solutions were prepared a series of single salt solutions, containing 0 to 0.10 *mM* of the anion in 20 ml of solution (series *A*) and a second series of mixtures containing known amounts of the analytes (series *B*).

Series *A* was used to determine the system heat pulse for the particular reactions, and series *B* was used to examine the validity of the concept of Partial Molar Heat Pulses when applied to mixtures of these anions.

Reagent solutions

The following were prepared and used as titrants: (a) 0.5 *M* silver nitrate solution; (b) saturated barium hydroxide solution; (c) 0.5 *M* sodium sulphide solution.

Determination of system heat pulses

A series of 10 aliquots each containing between 0.0 and 0.10 *mM* of the analyte per 20 ml of the sample was used in triplicate.

Where the molar heat of reaction was apparently zero, for a particular reaction [for example, arsenate(III) in its reactions with $Ba(OH)_2$ and Na_2S] binary and ternary systems were compared in order to assess the effect of an apparently non-reacting component on the heat pulses of the other analytes.

Results

Determination of insoluble phosphates in mixtures

The method was extended to the determination of insoluble phosphates and arsenate(V), by converting them to soluble sodium salts by metathesis with sodium carbonate. Weighed amounts (ca. 0.25 g) of known mixtures of freshly prepared and assayed calcium phosphate and magnesium arsenate(V) were mixed with 3 – 5 times their weight of anhydrous sodium carbonate and approximately 10 ml of water. The mixtures were boiled for approximately 10 minutes to ensure complete reaction, and were then filtered, the residues were later washed with 2 × 10 ml portions of boiling distilled water; the combined filtrate and washings were first acidified with 2 *M* HNO_3 and then boiled to remove any carbon dioxide.

System heat pulses for the single analyte

(1 *m*Mole of analyte in 20 ml of sample the sensitivity being 1 mV FSD)

Analyte	Reagents		
	Ag^+	Ba^{2+}	S^{2-}
Phosphate	750	150	175
Arsenate(V)	375	250	300
Arsenate(III)	300	Zero	Zero*

* See discussion

The pH of the resultant solution was adjusted to between pH 5 and 7 by dropwise addition of sodium hydroxide solution.

Determination of mixtures

(*a*) *Binary mixtures*

(*i*) *Determination of phosphate and arsenate*(*V*)

Reagents: Ag^+ and Ba^{2+}

Amounts of analytes in 20 ml of solution, in *mM*			
Added		Calculated	
phosphate	arsenate(V)	phosphate	arsenate(V)
0.010	0.100	0.010	0.100
0.020	0.080	0.020	0.080
0.040	0.060	0.039	0.060
0.060	0.040	0.060	0.040
0.080	0.020	0.079	0.020
0.100	0.010	0.099	0.010

(*ii*) *Determination of phosphate and arsenate*(*III*)

Reagents: Ag^+ and S^{2-}

Amounts of analytes in 20 ml of solution, in *mM*			
Added		Calculated	
phosphate	arsenate(III)	phosphate	arsenate(III)
0.010	0.100	0.010	1.100
0.020	0.080	0.020	0.078
0.040	0.060	0.040	0.061
0.060	0.040	0.060	0.040
0.080	0.020	0.080	0.020
0.100	0.010	0.100	0.010

(*iii*) *Determination of arsenate*(*V*) *and arsenate*(*III*)

Reagents: Ag^{2+} and S^{2-}

Amounts of analytes in 20 ml of sample, in *mM*			
Added		Calculated	
arsenate(V)	arsenate(III)	arsenate(V)	arsenate(III)
0.010	0.100	0.010	0.099
0.020	0.090	0.020	0.080
0.040	0.060	0.040	0.058
0.060	0.040	0.060	0.040
0.080	0.020	0.080	0.020
0.100	0.010	0.100	0.010

(b) *Ternary mixtures*

Determination of phosphate, arsenate and arsenite

Reagents: Ag^+, Ba^{2+}, S^{2-}

Amounts of analytes in 20 ml of sample, in *mM*

Added			Calculated		
phosphate	arsenate(V)	arsenate(III)	phosphate	arsenate(V)	arsenate(III)
0.020	0.040	0.060	0.020	0.040	0.060
0.040	0.060	0.020	0.040	0.060	0.018
0.060	0.020	0.040	0.060	0.020	0.040

The volumes were then made to 250 ml. 20 ml portions were used to ascertain the size of the heat pulses obtained and the solutions were then diluted approximately to give a heat pulse of between 100–150 mm.

Reproducibility of the determinations

Two series of 20 aliquots, each containing 0.040 *mM* phosphate and 0.060 *mM* of arsenate(V) per 20 ml were injected with either silver nitrate or barium hydroxide solution.

The standard deviation of the pulses obtained was determined for each series. The deviations were: For silver nitrate 1.25%; for barium hydroxide 1.35%.

Determination of mixtures containing calcium and magnesium salts

	Mixture	1	2	3	4
(a) Wt. of calcium phosphate, mg	added	251	176	141	–
	found*	249	174	140	–
(b) Wt. of magnesium arsenate(V), mg	added	–	78	116	254
	found*	–	80	118	251

* Calculated from triplicate determinations on the prepared sample solution

Discussion

It became evident during this and other similar investigations that it is necessary to standardize the system at the same temperature as that used for the actual determination since the sensitivity of the Wheatstone bridge when balanced depends to some extent upon the actual resistances in the four arms. Since one arm is a thermistor, whose resistance varies significantly with temperature change, the sensitivity of the bridge will vary with the temperature and subsequently the temperature pulse will apparently vary for the same heat change in the system; whilst this variation is small it is nevertheless an error which can be obviated by suitable experimental procedures. When the molar heat of reaction for a particular mixture of anions was apparently zero, it was considered necessary to investigate the possibility of co-precipitation and adsorption of the group(V) oxyanions; consequently the system heats of reaction for phosphate, for arsenate(V) with barium ions, and with sulphides were determined in the presence and in the absence of arsenate(III); no significant differences were obtained. Ternary mixtures of the three ionic species gave the same effects as did the binary mixtures without arsenate(III) present. It was thus concluded that arsenate(III) did not interfere in the reactions of the other species.

The kinetics of the reaction between sulphide and arsenate(III) ions are such that the reaction does not proceed to any significant extent during the time in which the injection is made and the solution reaches initial thermal equilibrium. After some time which depends to some extent on the relative concentrations of the arsenate(III) and the sulphide ion, a noticeable exothermic reaction commences, generally 20 to 30 seconds after the time of injection. This time delay is sufficient, using this technique to enable some selectivity to be obtained. The delay is not caused by the need for nucleation, since addition of a small amount of a suspension of arsenic(III) sulphide prior to the injection had no apparent effect on the delay.

It is interesting to note that there is apparently a reaction between phosphate and sulphide ions. Although it has been reported that the phosphate ion is very stable and has essentially no oxidising properties below 350 – 400°, and a search of the available literature did not indicate the possibility of a reduction between sulphide and phosphate, there is no doubt that a reaction of some type occurs. The nature of the reaction is being investigated but one problem associated with enthalpimetric reactions is that a large excess of one of the reactions is always present and hence it is not possible to follow any sequence of reactions by stepwise addition of one reactant and assume that these give the same products as those obtained by the enthalpimetric reaction.

We considered it essential to control the pH of the medium in order that any acid – base reactions between the medium and the added reactants would be practically zero, but nevertheless if present, would be manifested as constant parts of the heats of mixing of the barium hydroxide and the sodium sulphide solutions with the sample matrix. It was considered essential to keep the pH slightly below 7 in order to avoid precipitation of hydrated silver oxide on the addition of silver ions to the sample solution.

The metathesis of the calcium and magnesium salts was done using freshly prepared calcium phosphate and magnesium arsenate(V) in order to ensure comparability of results. Calcium phosphate which had been calcined gave varying results, probably as a result of incomplete metathesis. The problems associated with the metathesis of phosphates is under separate investigation.

From a consideration of the tests done on the reproducibility of the method it is suggested that the procedure gives results which are generally analytically acceptable in a relatively short time, and the method has potential for routine analysis of mixtures of the type tested. Work on mixtures containing other phosphate type anions in admixture is in progress.

*

One of us (AEN) acknowledges the provision of a Fellowship by UNESCO and leave by the University of Benin during the period when part of the work was done.

References

1. I. Sajó and B. Sipos, Radex Rundschau, 178 (1968).
2. P. Marik-Korda, L. Buzási and T. Cserfalvi, Talanta, 20 (1973) 569.
3. M. A. H. Al-Gifri and L. S. Bark, Proc. Soc. Anal. Chem., 13 (1976) 359.
4. P. Marik-Korda, Thermal Analysis, Proc. IVth ICTA, Akadémiai Kiadó, Budapest, 1974.
5. L. S. Bark and A. E. Nya, Anal. Chim. Acta (in press).
6. L. S. Bark and A. E. Nya, Thermochim. Acta (in press).
7. L. S. Bark and J. K. Grime, Analyst, 97 (1972) 911.
8. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 2nd Edition, Interscience Publishers, 1967, p. 152.

Résumé — On a analysé par enthalpimétrie une série de mélanges contenant chacun au moins deux des ions phosphate, arséniate(V) et arséniate(III), en utilisant le concept de l'additivité des impulsions de chaleur molaire partielle. La méthode a été appliquée à des réactions non sélectives comportant des précipitations et des réactions d'oxydo-réduction. A l'échelle de 1 *mM* l'exactitude est de 1.5% et la durée totale de l'analyse d'un mélange contenant les trois anions est inférieure à 10 minutes à partir de la mise en solution de l'échantillon. Dans le cas de phosphates insolubles, la mise en solution s'effectue par métathèse avec le carbonate de sodium.

Zusammenfassung — Eine Reihe von Gemischen, an denen jedes wenigstens zwei der Ionen Phosphat, Arsenat(V) und Arsenat(III) enthielt, wurde enthalpimetrisch unter Verwendung des Konzeptes der Additivität partialer molarer Hitzepulse bestimmt. Die angewandten nicht-selektiven Reaktionen umfaßten Fällungs- und Redox-Reaktionen. Bei der Größenordnung von 1 *mM* liegt die Genauigkeit innerhalb von 1.5% und die Gesamtzeit der Bestimmung einer alle drei Anionen enthaltenden Mischung beträgt weniger als 10 Minuten nach der Vorbereitung der Probenlösung. Diese wird im Falle unlöslicher Phosphate mittels Metathese mit Natriumcarbonat hergestellt.

Резюме — Ряд смесей, каждая содержащая по крайней мере два из таких ионов как фосфат, арсенат(V) и арсенат(III), были определены энтальпиметрически, используя концепцию аддитивности парциальных молярных теплот. Использовали неселективные реакции, включающие реакции осаждения и окисления-восстановления. Точность метода при содержании вещества в 1 ммоль была в пределах 1,5%, а общее время определения смеси всех трех анионов — меньше чем 10 мин после приготовления раствора образца, который для нерастворимых фосфатов получали реакцией обмена с карбонатом натрия.