Thermochimica Acta, 15 (1976) 301–305

THE ENTHALPIES OF SOLUTION OF POTASSIUM CHLORIDE AND 2-AMINO-2-(HYDROXYMETHYL)-1,3-PROPANEDIOL (TRIS)

K. H. GAYER AND P. S. KOTHARI*
Department of Chemistry, Wayne State University, Detroit, Mich. 48202 (U.S.A.)
(Received 25 September 1975)

ABSTRACT

The performance of 2-amino-2-(hydroxymethyl)-1,3-propanediol (Tris) and potassium chloride as solution calorimetry comparison standards has been evaluated. It has been established that both of these have some drawbacks, but of the two, we believe Tris is the preferable calorimeter comparison standard.

INTRODUCTION

The heat of solution of potassium chloride[1–3] has most often been proposed as a comparison standard. However, the results show poor agreement. Sunner and Wadso[4] have questioned the suitability of potassium chloride as a primary standard because of the high temperature coefficient of the enthalpy of solution at room temperature (36 cal deg^{-1} mol^{-1}) and the relatively low molar enthalpy of solution. The results are influenced by minute amounts of impurities and size of crystals. When used in connection with a measured reaction having a large temperature change, a large amount of potassium chloride must be used resulting in a high solution concentration and a high differential heat of solution.

Wadso and Irving[5] in 1963 proposed the use of solid 2-amino-2-(hydroxymethyl)-1,3-propanediol or Tris (hydroxymethyl)aminomethane, referred to as Tris hereafter, with excess aqueous hydrochloric acid. Tris has properties qualifying it as a primary acidimetric standard[6].

In 1964 the Calorimetry Conference asked the U.S. National Bureau of Standards to prepare a large, uniform batch of Tris and make it available to various laboratories. In 1967 NBS Standard Reference material 724 "Solution Calorimetry Standard" was distributed to selected laboratories including this laboratory.

Gunn[7] compared the performance of four reference standards, potassium chloride, Tris–HCl, sulfuric acid–sodium hydroxide and succinic acid–hydrochloric acid. His results, however, were not conclusive.

---

*Present address: Chemical Abstracts, Columbus, Ohio (U.S.A.)

EXPERIMENTAL

Preparation of materials

Potassium chloride from Matheson, Coleman and Bell Co. reagent grade material was screened through a 200 mesh sieve, dried at 140°C in an oven and stored over phosphorous pentoxide in a vacuum desiccator.

Two samples of Tris were used. One sample received from National Bureau of Standards, "Reference Material 724", was stored over a saturated solution of magnesium nitrate which provides 50% relative humidity. The other sample of Tris was Matheson, Coleman and Bell Co. reagent grade material. This sample was dried in an oven at 80°C and stored over calcium chloride in a vacuum desiccator.

Reagent grade Baker and Adamson hydrochloric acid diluted with carbon dioxide free double distilled water was used as the solvent for Tris. The strength of the hydrochloric acid solution was adjusted to 0.1 M. For the potassium chloride work, carbon dioxide free double distilled water was used as solvent.

Weighings were corrected to "in vacuo", using the density of 1.98 g cm^{-3} for potassium chloride and 1.35 g cm^{-3} for Tris. A known volume (350 or 400 ml) of solvent, carbon dioxide free boiled double distilled water for potassium chloride and 0.1M hydrochloric acid for Tris, precooled to a few tenths of a degree below the jacket temperature was transferred to the calorimeter vessel. All reactions were run near 25°C. To avoid errors due to condensation the temperature of the calorimeter was not allowed to rise above the jacket temperature.

One or more electrical calibration runs were made in the same temperature range before and after each reaction run.

Calorimeter

The precision solution calorimeter was patterned after that described by Busey et al.[8] with modifications described by Busey et al.[9]. Briefly it is of the semi-adiabatic

TABLE I

ENERGY EQUIVALENT OF THE CALORIMETER (including 450 ml of water)
Standard deviation = 2.576; percent deviation = 0.127; C_p (calorimeter) = 2029.858 − 1875.31 ($n_{H_2O}C_pH_2O$) = 154.55 J.

No.	*EIT* (*J*)	ΔT (°*C*)	$C_p + n_{H_2O}C_{pH_2O}$ (*J deg*$^{-1}$)
1	141.612	0.069795	2029.100
2	148.025	0.072940	2029.277
3	102.786	0.050497	2035.361
4	102.506	0.050461	2031.236
5	133.603	0.065792	2030.511
6	155.535	0.076621	2029.887
7	102.077	0.050354	2027.056
8	102.843	0.050747	2026.438
		Average	2029.858

type having an isothermal jacket. It has a usable volume of 450 cm^3 and an energy equivalent of 154.6 ± 1.9 J (36.95 cal). Data details are shown in Table 1.

DATA AND DISCUSSION

Precision of the calorimeter

Results of the energy equivalent of the calorimeter given in Table 1 show internal agreement within ±0.127%. For the heat of solution of KCl given in Table 2,

TABLE 2

HEAT OF SOLUTION OF POTASSIUM CHLORIDE

Standard deviation = 0.0565; percent deviation = 0.32%.

No.	*KCl* *(mol)* $\times 10^{-3}$	*Water* *(mol* mol^{-1} *KCl)*	T_{mean} (°C)	ΔH *(kJ* mol^{-1}*)*
1	8.07055	2396	24.9156	17.659
2	8.79756	2198	24.9526	17.534
3	7.31540	2678	25.0001	17.540
4	7.83700	2500	24.9616	17.636
5	7.28456	2690	24.9016	17.583
6	8.66100	2263	25.1003	17.502
			Average	17.576.2

TABLE 3

HEAT OF SOLUTION OF 2-AMINO-2-HYDROXYMETHYL-1,3-PROPANEDIOL (TRIS)

No.	*Tris* *(mol)* $\times 10^{-2}$	*Water* *(mol* mol^{-1} *Tris)*	T_{mean} (°C)	ΔH *(kJ* mol^{-1}*)*
			NBS sample	
1	1.5449	1426	24.9690	29.696
2	1.6552	1331	25.0784	29.855
3	1.6221	1358	25.0373	29.750
4	1.6497	1335	25.0433	29.776
			Average	29.769
			Standard deviation	0.0573
			Percent deviation	0.19%
			Matheson, Coleman and Bell sample	
1	0.5419	3558	24.8752	29.463
2	0.5145	3747	25.1069	29.727
3	0.3692	5222	25.0878	29.933
4	0.5666	3402	25.0932	29.952
5	0.5522	3492	25.0449	29.635
			Average	29.742
			Standard deviation	0.184
			Percent deviation	0.61%

the internal agreement is within ±0.32%. Similarly for the heat of solution of Tris given in Table 3 the internal agreement is within ±0.19% for the National Bureau of Standards sample and ±0.61% for the Matheson, Coleman and Bell sample. The higher range of error for Matheson, Coleman and Bell sample could be due to variations of grain size or due to impurities. All these results indicate the high precision of the calorimeter.

Accuracy of the calorimeter

Accuracy of the calorimeter can be ascertained by comparison with the best available literature values:

ΔH solution	*Gunn*[7] *(kJ mol^{-1})*	*Wadso*[5] *(kJ mol^{-1})*	*Present work (kJ mol^{-1})*
KCl	17.5744		17.5762
$(CH_2OH)_3C\ NH_2$	29.742	29.744	29.738

Potassium chloride as calorimeter comparison standard

As a calibration standard potassium chloride has several disadvantages but as Gunn has pointed out the spread in values reported in the literature of up to 2% is surprising. He has suggested that a uniform batch of this material be prepared by the National Bureau of Standards and distributed to various laboratories. The main disadvantages, however, still remain. The material has a comparatively low molar heat of solution and a high temperature coefficient of heat of solution requiring temperature corrections involving uncertainties in various heat capacities.

2-Amino-(2-hydroxymethyl)-1,3-propanediol as calorimeter comparison standard

Tris does not suffer from the above disadvantages but it often has a troublesome time-lag of 50–90 sec between the release of sample and initiation of reaction. This results in an uncertainty as to the end of the initial rating period and beginning of the main period in the graphical extrapolation. Storing the sample at room temperature in a desiccator over a saturated magnesium nitrate solution, which provides 50% relative humidity, helps partially in overcoming this lag.

ACKNOWLEDGMENT

The authors wish to express their gratitude to the Atomic Energy Commission (Grant Numbers AT-(1101)-1065 and AT-(11-1)-214 for their interest and financial support of this research.

REFERENCES

1 K. P. Mischenko and Y. Y. Kagonovich, *Zh. Prikl. Khim.*, 22 1078 (1949).
2 G. Samsen, J. Coops and M. W. Tolk, *Rec. Trav. Chim.*, 82 (1963) 231.

3 V. B. Parker, *N. B. S. Report*, NSRDS-NBS-2, 1965.
4 S. Sunner and I. Wadso, *Acta Chem. Scand.*, 13 (1959) 97.
5 I. Wadso and R. J. Irving, *Acta Chem. Scand.*, 18 (1964) 195.
6 J. H. Fossum, P. C. Markunas and J. A. Ridduk, *Anal. Chem.*, 23 (1951) 491.
7 S. R. Gunn, *J. Phys. Chem.*, 69 (1965) 2902.
8 R. H. Busey, H. H. Dearman and R. B. Beven, Jr., *J. Phys. Chem.*, 66 (1962) 82.
9 R. H. Busey, K. H. Gayer, R. A. Gilbert and R. Beven, Jr., *J. Phys. Chem.*, 70 (1966) 2609.