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Resolution of a systematic interlaboratory discrepancy in recent calorimetric data, and the heats of solution of quartz, low albite, adularia, and gibbsite

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Abstract

Based on enthalpies of solution of quartz, low albite, adularia, and gibbsite, solution calorimetric data presently being collected at Lafayette College are in excellent agreement with those from the thermochemistry laboratory of the USGS and other solution calorimetry laboratories. However, calorimetric data collected on this same equipment during its operation at Harvard University prior to 1974 are systematically different from the present results. Electrical resistance associated with lead wires in the heater circuit of the calorimetric system accounts for the discrepancy. As a result, all enthalpies of solution measured on the Harvard system (and incorporated in publications through 1977) must be multiplied by 0.9895. This will enable *corrected* Harvard data to be used in conjunction with calorimetric data from other laboratories. Rewiring of the heater circuit and tests against a standard resistor have resulted in the better agreement presently observed between Lafayette data and those of other laboratories.

Background and explanation

Data produced from the solution calorimetric system at Lafayette College are systematically different from data produced by the same system during its operation prior to 1974 at Harvard and Princeton Universities. Data collected since 1978 are in closer agreement with data from the thermochemistry laboratory at the United States Geological Survey (USGS) in Reston, Virginia, operated by R. A. Robie and B. S. Hemingway, with data from the National Bureau of Standards (NBS), and with data from other solution calorimetric laboratories. The purposes of this manuscript are to explain the differences between early calorimetric data produced on this system and present values, to clarify interlaboratory discrepancies which have existed until now, and to minimize the chances for confusion when new data are published in the future.

In 1967 money was granted to Harvard University to build a solution calorimetric system (hereafter referred to as the Harvard system, and the data as Harvard data), initially to measure enthalpies of mixing and enthalpies of polymorphic transitions in the alkali feldspars. After the Harvard system was put into operation, it became evident that there was a systematic discrepancy between the absolute values of Harvard enthalpies of solution and those of the USGS in Reston, Virginia. While each laboratory produced internally consistent data (that is, enthalpy *differences* among minerals were the same within experimental error), the *absolute values* of Harvard enthalpies of solution were between 1 and 2% higher than those of the USGS laboratory. This discrepancy was incorporated in data published in several papers (Hovis, Thompson, and Waldbaum, 1970; Hovis, 1971 and 1974; Thompson, Waldbaum and Hovis, 1974; Hovis and Waldbaum, 1977) and was referred to in a number of these.

After a short period of operation at Princeton University, and after the death of D. R. Waldbaum, the calorimetric system was moved to Lafayette College. At this time I felt that it was necessary to resolve the discrepancy that existed.

Testing procedures

During solution calorimetric runs, voltage measurements are made on (1) a heater circuit and (2) a thermometer circuit (see Hovis, 1971; also Robie and Hemingway, 1972). Both voltage and current (measured as the voltage across a series standard resistor) of these circuits can be measured. In the case of the heater circuit, knowledge of voltage, current, and the amount of time during which heating takes place makes it possible to calculate the amount of electrical energy put into the calorimeter during the determination of its heat capacity. In the case of the thermometer circuit, voltage and current data are used to calculate resistance, which in turn is correlated with temperature, this in order to detect temperature changes during an experiment. Obviously measurements of voltage and current on these circuits must be accurate in order to obtain good results.

By substituting a standard resistor in place of the calorimeter it is possible to check the accuracy of measurements on both the heater and thermometer circuits. This procedure had been followed with the USGS calorimetric system, and as a first step in resolving the interlaboratory discrepancy the same was done on the Harvard system. With the help of B. S. Hemingway measurements were made on the heater circuit with a Guildline 100-ohm standard resistor in place of the calorimeter. Based on voltage and current measurements during heating, the calculated resistance of 98.972 ohms was about 1% different from the value of 100.0001 ohms given for the standard resistor. This was apparently the major source of error in the Harvard measurements.

To rectify this problem Hemingway and I changed the electrical connections in the heater circuit. The four lead-wire system, which before had been connected only indirectly via a terminal strip to the one-ohm standard resistor in the heater circuit, was reconnected directly to the standard resistor terminals. Based on voltage and current measurements after this modification, the calculated resistance of 99.948 ohms was only 0.05% different from the 100.0001 ohm value given for the standard resistor substituted for the calorimeter. Obviously series lead resistance had led to an error which was significant relative to the resistance of the one-ohm standard resistor across which current values were determined.

Similar procedures were used to check the thermometer circuit. Initial calculated resistances on this circuit, however, were in much better agreement because the standard resistor across which current values were determined was a 100-ohm resistor, not a one-ohm resistor. Nevertheless, as with the heater circuit, wires were reconnected directly to the standard resistor terminals. Calculated resistances of the substitute 100-ohm resistor after this change were slightly improved and different from 100 ohms by less than 0.1%. It is not possible that the latter change would account for a major part of the discrepancy between the Harvard and the USGS data because (1) series lead resistance would not have been significant compared to the 100-ohm standard resistor across which current measurements were determined and (2) a significant part of any such discrepancy would have canceled out since it is temperature *differences* that are critical in calculating heats of solution.

In summary, measurement errors in the heater circuit were the principal reason for the discrepancy between Harvard calorimetric data and those of other calorimetric systems. These errors resulted in calculated calorimetric heat capacities about 1% higher than the correct values; in turn, absolute values of the heats of solution were also about 1% too high. This also accounts for the fact that enthalpy *differences* among minerals (especially feldspars) were quite similar to those of the USGS. Here, too, much (though not all) of the discrepancy canceled out in subtraction, as long as Harvard data *only* were used to calculate these differences.

Results of recent calorimetric measurements

Since modifying our solution calorimetric system, I have measured heats of solution on a number of substances in order (1) to determine the relationship between the older data collected at Harvard University and the newer data collected at Lafayette College since modification and (2) to compare data now being collected with those of the USGS and other solution calorimetry laboratories. Comparison of Harvard data with those collected since the modification is made in Table 1. All experiments were conducted in 20.1% HF at 50° (±0.3°) C under isoperibolic conditions. Comparison with data from other solution calorimetry laboratories is made in Table 2.

Quartz

The enthalpy of solution of quartz varies with temperature of dissolution, acid composition, and the grain size of the starting material (Kilday and Prosen, 1973; Hemingway and Robie, 1977; Hemingway, personal communication). In order to compare calorimetric results to those of other laboratories, it is best to use the same type of sample material used by those laboratories, and to do experiments under the same acid and temperature conditions. Fortunately the National Bureau of Standards has made available SRM-1654, natural Brazilian quartz with grain size that "passes a #200 sieve but is retained on a #400 sieve," according to

Table 1. Solution calorimetric data on quartz, Amelia low albite, adularia, and gibbsite based on measurements made at Harvard University prior to 1974 and on measurements made at Lafayette College since 1978

	Run*	Mass(g)	ΔT(°C)†	Mean Solution T(°C) (IPTS-68)	Heat Capacities (cal/deg)	Heats of Solution (J/g)	Heats of Solution†† (kcal/mol)	Average Heats of Solution (J/g & kcal/mol)	Correction Factor to Harvard Data
Quartz	H-172**	1.00126	0.598253	49.909	925.61, 926.28	-2312.85, -2315.36	-33.214, -33.250	-2314.4 ±1.5 -33.237 ±.022	Quartz 0.9897
	H-245	0.84713	0.521059	49.935	899.81, 899.49	-2314.60, -2314.53	-33.239, -33.238		
	H-247	0.87073	0.536938	49.941	897.92, 898.22	-2315.64, -2317.17	-33.254, -33.276		
	H-249	0.80830	0.496624	49.959	900.19, 899.61	-2313.06, -2312.23	-33.217, -33.205		
	L-359	1.00171	0.615757	49.970	889.70, 892.32	-2288.64, -2294.60	-32.866, -32.952	-2290.6 ±5.8 -32.895 ±.083	
	L-360	1.01318	0.623848	49.507	889.60, 891.41	-2292.21, -2296.09	-32.918, -32.973		
	L-362	1.00871	0.617737	50.010	889.39, 892.00	-2279.27, -2285.17	-32.732, -32.817		
	L-376	0.75152	0.461465	49.800	892.94, 893.18	-2294.41, -2294.43	-32.949, -32.949		
Amelia Low Albite	H-163**	1.00026	0.623515	50.382	926.59, 926.09	-2416.32, -2414.18	-151.531, -151.396	-2418.5 ±2.6 -151.665 ±.164	Amelia Low Albite 0.9890
	H-164**	1.00135	0.624784	50.255	926.64, 928.11	-2418.74, -2421.73	-151.682, -151.870		
	H-165**	1.01220	0.632126	49.929	925.77, 927.06	-2418.67, -2421.17	-151.678, -151.835		
	L-379	0.50192	0.322256	49.940	890.00, 890.61	-2391.16, -2392.16	-149.953, -150.015	-2391.9 ±0.8 -149.999 ±.051	
	L-380	0.50180	0.322286	49.959	890.16, 890.64	-2392.42, -2393.05	-150.032, -150.071		
	L-382	0.49263	0.316410	49.956	889.40, 890.30	-2390.41, -2392.20	-149.906, -150.018		
Adularia 7007	H-254	0.94879	0.565990	50.005	898.92, 899.78	-2243.30, -2244.73	-148.026, -148.120	-2242.4 ±1.6 -147.963 ±.104	Adularia 0.9897
	H-256	0.81513	0.486684	49.964	897.45, 898.27	-2241.60, -2242.94	-147.914, -148.002		
	H-257	0.95046	0.567445	50.010	896.45, 897.83	-2238.96, -2241.67	-147.739, -147.918		
	H-259	0.78127	0.466709	49.837	897.59, 897.64	-2243.09, -2242.55	-148.012, -147.976		
	L-377	0.51487	0.306672	49.898	890.24, 890.69	-2220.11, -2220.64	-146.495, -146.530	-2219.3 ±0.9 -146.442 ±.061	
	L-378	0.50870	0.303109	49.940	889.76, 889.99	-2218.52, -2218.51	-146.390, -146.391		
	L-381	0.50322	0.299731	49.927	889.97, 890.87	-2218.20, -2219.84	-146.370, -146.478		
Gibbsite A-581	L-341	1.00840	0.548169	49.980	889.91, 892.43	-2024.37, -2029.46	-37.741, -37.836	-2027.8 ±1.8 -37.805 ±.034	--
	L-347	0.99680	0.541968	49.835	890.98, 891.52	-2027.21, -2027.78	-37.794, -37.805		
	L-349	1.01015	0.549438	49.940	890.77, 890.83	-2027.50, -2026.99	-37.799, -37.790		
	L-364	1.00136	0.544973	49.996	889.84, 892.45	-2026.56, -2031.85	-37.782, -37.880		
	L-396	1.00407	0.546637	49.936	889.51, 891.12	-2026.49, -2029.52	-37.781, -37.837		
	L-397	1.00086	0.544678	49.881	889.94, 891.19	-2026.71, -2028.89	-37.785, -37.825		

* *All runs prefixed by "H" were done at Harvard University; runs prefixed by "L" were done at Lafayette College after modification of the calorimetric system. All runs in 910.1 g of acid, except as noted by double asterisk. Acid composition 20.1 weight % HF.*

***Run conducted in 940.1 g of acid.*

† *Temperature change during dissolution period.*

†† *Molar heats of solution for Amelia low albite assume a composition of N_{or} = 0.0099, gfw = 262.3840; molar heats of solution for adularia assume N_{or} = 0.8602, gfw = 276.0842.*

Table 2. Summary of solution calorimetric data on quartz, Amelia low albite, and gibbsite from various laboratories

Substance	Average Heats of Solution (J/g) from:		
	Lafayette College (Since 1978)	U.S. Geological Survey Thermochemistry Laboratory Reston, Virginia	National Bureau of Standards
QUARTZ	-2290.6	-2264.9	-2309.9†
AMELIA LOW ALBITE	-2391.9	-2393.5* -2398.8**	--
GIBBSITE	-2027.8	-2014.7***	--

* *Calculated from data in Waldbaum and Robie (1971, Table 5; specimens 6314, 6306, and 6321 but excluding data for grain sizes less than 400 mesh).*

** *Calculated from data in Hemingway and Robie (1977).*

****Calculated from Hemingway, Robie, and Kittrick (1978; Hemingway, personal communication).*

† *Calculated from data on certificate enclosed with National Bureau of Standards standard reference material 1654, measurements made by Kilday and Prosen (1971; also see 1973). Value given uses first equation on the certificate to correct NBS data to 50°C and assumes that correction for acid composition (second equation on the certificate) is valid for 50°C, as well as for 80°C.*

the certificate received with the NBS sample. Apparently, however, particle size does vary among different bottles of this material. Also some bottles do contain −400 mesh grains. This can affect heats of solution by up to 7 J/g (Hemingway, personal communication). Nevertheless, measurements have been made on SRM-1654 in our own laboratory since modification of our system, as well as at the National Bureau of Standards (Kilday and Prosen, 1973) and at the United States Geological Survey in Reston, Virginia (Hemingway and Robie, 1977).

The certified heat of solution given by NBS for SRM-1654 is −2362.2 J/g. However, this value applies to dissolution done at 80° C in 24.4% hydrofluoric acid. Dissolutions also were made at other acid compositions and temperatures, and equations given on the NBS certificate allow for corrections to the data based on temperature and acid composition. If NBS data are adjusted so as to correspond to 50° C and 20.1% HF, a value of −2309.9 J/g is obtained.

Hemingway and Robie (1977) have measured the enthalpy of solution of SRM-1654 in 20.1% HF, but at temperatures of 60° and 75° C. A linear least-squares fit of their data produces an extrapolated enthalpy of solution of −2264.9 J/g for 50° C. The average heat of solution for this material measured at Lafayette College (−2290.6 J/g) is midway between the values above based on NBS and USGS data.

There is not good agreement on the dependence of the heat of solution of quartz on temperature and acid composition. The temperature coefficient obtained from the least-squares fit of the Hemingway and Robie (1977) data (−2.744 J/g-deg.) is nearly twice the NBS value (−1.586 J/g-deg., Kilday and Prosen, 1973) for the corresponding coefficient. The NBS correction for acid composition is slightly curved but has an average slope that is less than one-fourth that determined by Hummel and Schwiete (1959; based on other samples of α-quartz) from their measurements made at 26.45° C. Obviously these uncertainties make it possible to extrapolate the heats of solution so as to obtain the desired result, but this does not test the accuracy of the calorimetric results, which is the point at issue here. It does seem, however, that our value is in reasonable agreement with data from other solution calorimetry laboratories (for example, Kilday and Prosen, 1973, and Hemingway and Robie, 1977).

It must be noted that the quartz sample used at Harvard University was not SRM-1654. However, it was of a quality and grain size comparable to SRM-1654. It is very unlikely that any differences between the two quartz specimens could account for the Harvard data (−2314.4 J/g), which are about 1% higher in absolute value than Lafayette data.

Amelia low albite

The material used by the Harvard and the Lafayette laboratories for measurements on low albite came from a batch of crystals collected personally by D. R. Waldbaum at Amelia Courthouse, Virginia. This is the same material used by Waldbaum in his dissertation research (Waldbaum, 1966) done at the USGS in the mid-1960's with Robie and published in Waldbaum and Robie (1971). Measurements also have been made on this material by Hemingway and Robie (1977; data points six, twelve, thirteen, and fifteen under "low albite" in their Table 3); the latter authors in addition have made measurements on another sample of Amelia low albite supplied by Stewart (data points seven and eight of the same table). All measurements by us and by Waldbaum (1966) were made at 50° C, while those of Hemingway and Robie (1977) were made at temperatures of 50° and 60° C.

As with quartz the Lafayette heats of solution (−2391.9 J/g) are lower in absolute value, by slightly more than 1%, than the Harvard data (−2418.5 J/g). The former value is in excellent agreement with the value calculated (−2393.5 J/g) from Table 5 of Waldbaum and Robie (1971). (Values given in Table 5 for −400 mesh material were omitted from the calculations because of possible grain-size effects, though this omission made virtually no difference in the average heat of solution.) A least-squares fit to the data of Hemingway and Robie (1977) as a function of temperature indicates no temperature dependence for their heats of solution. This fit, based on six experiments, yields a value of −2398.8 J/g for their dissolutions, while the average value for their two 50° C measurements is −2400.0 J/g. Lafayette data are now in excellent agreement with the data of Waldbaum and Robie (1971) and very close to the data of Hemingway and Robie (1977).

Adularia

A further comparison can be made between the Harvard and the Lafayette systems based on data for adularia 7007, described (Hovis, 1971 and 1974) as a highly ordered (in terms of Al/Si distribution) monoclinic potassium-rich feldspar from St. Gotthard, Switzerland. The structure of this material has been determined by single crystal X-ray diffraction techniques (Phillips and Ribbe, 1973), and a recent chemical analysis indicates that it has a K/K + Na ratio of 0.8602. Results of Lafayette calorimetric measurements (−2219.3 J/g) again are slightly more than 1% lower in absolute value than the Harvard results (−2242.4 J/g).

Aluminum hydroxide

Hemingway *et al.* (1978) have reported the enthalpies of solution of several samples of gibbsite at 30° C, and they present data for temperatures to 73.7° C. As a further check on the Lafayette calorimetric system, six measurements of the enthalpy of solution of reagent grade aluminum hydroxide were made at 50° C. The material used in our investigation was reagent A-581 from Fisher Scientific Company; this reagent was one of the materials used by Hemingway *et al.* (1978) in their study, though our sample did not come from the same jar of material as theirs. Our average value of −2027.8 J/g compares favorably with the value of −2014.7 J/g calculated for 50° C in Figure 1 of Hemingway *et al.* (1978). The data presented by these authors show that a scatter of ±20 J/g (apparently due to poor crystallinity and/or the presence of other aluminum hydroxide phases in the starting material) is not unrealistic for a gibbsite sample such as the reagent grade material used in this study (also Hemingway, personal communication). The difference between the average values of the two laboratories is well within this uncertainty.

Conclusions

It is evident from Table 1 and from the previous discussion that enthalpies of solution determined from experiments conducted at Harvard University prior to 1974 (and incorporated in publications through 1977) must be corrected. Solution calorimetric experiments on three distinctly different materials (quartz, Amelia low albite, and adularia) produce correction factors to the Harvard data which are very consistent. An average of the correction factors in Table 1 indicates that previously reported enthalpies of solution (Hovis, Thompson, and Waldbaum, 1970; Hovis, 1971 and 1974; Thompson, Waldbaum, and Hovis, 1974; Hovis and Waldbaum, 1977) should be multiplied by a factor of 0.9895 (±0.0004). This will enable the corrected enthalpies of solution from Harvard to be used in future calculations which involve calorimetric data from other laboratories, particularly data of the USGS, as well as from the present calorimetric system at Lafayette College.

Enthalpies of solution presently being collected in our laboratory are in good agreement with those of other solution calorimetry laboratories (see Table 2). In particular our results on Amelia low albite are virtually identical to those of Waldbaum and Robie (1971) and very close to those of Hemingway and Robie (1977), while data on quartz and gibbsite are within the scatter observed for different samples of these materials. I shall be interested in continuing cooperation with other laboratories to assure consistency among our results.

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