

## ENERGY STORAGE CAPACITIES OF REVERSIBLE LIQUID PHASE CHEMICAL REACTIONS

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### ABSTRACT

The heat capacity, and thus energy storage capacity of a liquid mixture may increase due to chemical reaction. This is illustrated with methanol-butyr-aldehyde mixtures. The volumetric heat capacity of an equimolar *n*-butyr-aldehyde-methanol mixture would be  $0.47 \text{ cal ml}^{-1} \text{ }^{\circ}\text{C}^{-1}$  if no reaction occurred. The experimental value is 0.99 over the temperature range of 20 to  $46^{\circ}\text{C}$ .

### INTRODUCTION

Consider the reaction,  $A + B \rightarrow C$ , which is reversible, occurs in the liquid phase, and is exothermic with the generation of C. The amount of C at equilibrium decreases with increasing temperature. Such a reaction might be attractive for energy storage schemes [1,2] because heat can be stored as a heat of reaction, as well as sensible heat. In a solar energy system, for example, the temperature of the reaction mixture would increase during the day, with the simultaneous decomposition of C. The decomposition process itself would store energy. At night heat would be retrieved from the mixture. The temperature would decrease with the simultaneous formation of C. The net effect of the reaction would be to increase the apparent heat capacity of the liquid phase mixture. In energy storage applications, it is desired to store a large amount of energy in a small space. Thus, the desired property for evaluation of the energy storage capacity of a reaction mixture is its volumetric heat capacity.

Many techniques are not well suited for evaluating a reaction's energy storage capacity. Calculation of the storage capacity requires equilibrium constant and heat of reaction data that are often not available. For a reaction to successfully store energy, the compound, C, must easily decompose to A and B, so conventional analysis techniques often do not work. Gas chromatography, for example, is not suitable for determining concentrations of C because C decomposes when subjected to even moderate injection temperatures.

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Calorimetry is ideally suited for determining a reaction mixture's energy storage capacity and in this paper experimental values of volumetric heat capacities are presented for two classes of reactions. The first is addition of sodium bisulfite to aldehydes and ketones; the second is addition of methanol to normal and isobutyraldehyde to form the resulting hemiacetal [3]. Equilibrium constant and heat of reaction data have been reported for most of the reactions studied [4,5]. Although these data are for conditions different from those used in this study, they do allow calculation of volumetric heat capacities for comparison with experimental results.

A home-made calorimeter was used to measure volumetric heat capacities to  $\pm 3\%$  for mixtures in which a chemical reaction could occur. Greater precision is possible with more sophisticated equipment, but the stated precision is sufficient to demonstrate that reaction can significantly increase the energy storage capacity of a liquid mixture. Furthermore, the calorimeter design allowed for rather large temperature changes over extended periods of time in concentrated solutions. These conditions more closely approximate the situation in an actual energy storage scheme, and also provided sufficient time for the reaction mixture to reach chemical equilibrium. To measure the heat capacity, a known amount of heat was added to the solution and the resulting temperature change measured. Calibration data were first obtained with materials for which thermal properties were sufficiently well known to allow a determination of the calorimeter heat capacity and heat losses. These calibration data plus measurements on the reacting mixtures gave the desired values of the volumetric heat capacities.

The calorimeter and its lid were made of aluminum. The calorimeter had a volume of 300 ml and weighed 860 g. In a typical run, the solution was placed in the vessel and pressurized with nitrogen to 40 psig. This minimized vaporization, even though large vapor pressure changes could result from the large temperature changes. The vessel was insulated with a two inch-close fitting styrofoam shell. The solution was stirred with a magnetic stirring bar and the temperature in the solution was measured with a six junction, copper-constantan thermopile.

To initiate a measurement, the solution, at room temperature, was placed in the calorimeter, also at room temperature. After an additional 6-minute temperature equilibration period, the heater was turned on for a 24-minute heating period. The solution temperature was recorded 9 min later, or 39 min after the start of the cycle. This 9-minute period was sufficient for the reactions in this study to reach their equilibrium concentrations. Increasing the 9 min to 30 min did not affect the final results. A typical heating cycle which was for the 50 wt.% propanol calibration solution is shown in Fig. 1. The cycle was repeated 8 to 16 times for each of the five calibration solutions listed in Table 1 and three times for each of the seven reaction mixtures listed in Table 2.

The heat input for each heating cycle,  $Q_{in}$ , was nominally 12,190 cal. A portion of  $Q_{in}$ ,  $Q_{soln}$ , was absorbed by the solution and a portion,  $Q_{loss}$ , was either absorbed by the calorimeter or lost to the surroundings. For the calibration solutions,  $Q_{soln}$  was calculated using the known thermal properties in Table 1 along with the experimental  $\Delta T$ , where  $\Delta T$  is the temperature of the solution 39 min after the start of a cycle

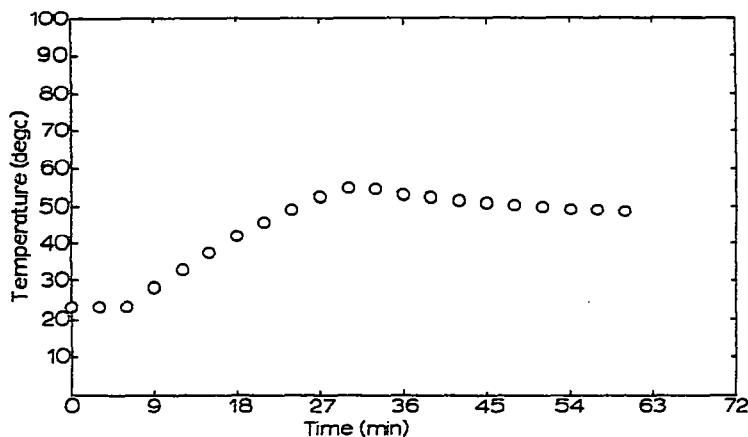


Fig. 1. Typical heating cycle showing initial equilibration period, heating period, and the final equilibration period.

minus the initial temperature.  $Q_{\text{loss}}$  was then calculated by

$$Q_{\text{loss}} = Q_{\text{in}} - (MC_p)_{\text{soln}} \Delta T \quad (1)$$

where  $M$  is the mass of solution. This procedure led to the calibration curve, Fig. 2, which gives the heat absorbed by the calorimeter,  $Q_{\text{loss}}$ , vs.  $\Delta T$ . The least-square line shown in Fig. 2 passed through the 90% confidence interval for all five calibration solutions. The equation of this line is  $Q_{\text{loss}} = 321 \Delta T - 3290$ , where  $Q_{\text{loss}}$  is in cal and  $\Delta T$  is in  $^{\circ}\text{C}$ . Substitution into eqn. (1) gives

$$(MC_p)_{\text{soln}} = \frac{Q_{\text{in}} + 3290}{\Delta T} - 321 \quad (2)$$

To determine  $MC_p$  for the reaction solutions,  $Q_{\text{in}}$  and  $\Delta T$  at 39 min were measured three times for each of the seven solutions.  $MC_p$  for each solution was obtained from eqn. (2). Experimental densities were then used to convert values of  $MC_p$  to volumetric heat capacities.

TABLE I

Calibration solutions and their physical properties [6,7,8]

Solution	Density at 20 $^{\circ}\text{C}$ (g ml $^{-1}$ )	Heat capacity constants	
		$a \times 10^4$	$b$
Water	0.994	0.0	0.999
50 wt. % propanol in H $_2$ O	0.905	9.2	0.876
70 wt. % propanol in H $_2$ O	0.864	18	0.742
Propanol	0.800	30	0.465
Heptane	0.688	9.4	0.513

$C_p = a + bT$ ,  $C_p$  in cal g $^{-1}$   $^{\circ}\text{C}^{-1}$ ,  $T$  in  $^{\circ}\text{C}$ .

TABLE 2  
Summary of reaction conditions and final results

Reactants with initial mole fractions <sup>a</sup>	Density (g ml <sup>-1</sup> )	Volumetric heat capacity (cal ml <sup>-1</sup> °C <sup>-1</sup> )		
		Calculated without reaction	Calculated with reaction	Experimental
Methyl ethyl ketone 0.041 + NaHSO <sub>3</sub> 0.082	1.25	0.965	0.975	1.00
Acetone 0.044 + NaHSO <sub>3</sub> 0.088	1.27	0.972	0.974	0.96
Ethyl acetoacetate 0.050 + NaHSO <sub>3</sub> 0.100	1.31	0.924	0.934	0.91
<i>n</i> -Butyraldehyde 0.033 + NaHSO <sub>3</sub> 0.069	1.22	0.970	0.970	1.00
<i>i</i> -Butyraldehyde 0.023 + NaHSO <sub>3</sub> 0.044	1.15	0.987		0.98
<i>i</i> -Butyraldehyde 0.500 + methanol 0.500	0.858	0.520	0.766	0.96
<i>n</i> -Butyraldehyde 0.500 + methanol 0.500	0.872	0.467	0.824	0.99

<sup>a</sup> Water was the solvent for the sodium bisulfite reactions.

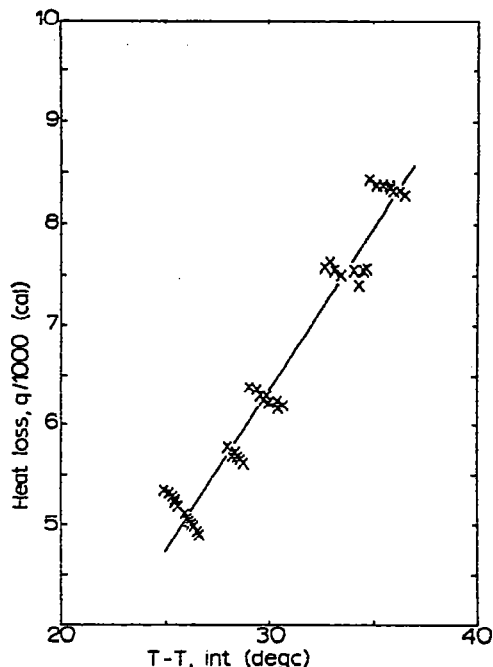


Fig. 2. Calibration plot of the heat lost to the calorimeter after 39 min vs.  $\Delta T$  of the solution. The line is a least square fit of all points.

## RESULTS AND DISCUSSION

Volumetric heat capacities for seven different reaction mixtures are summarized in Table 2. Experimental values were determined by the procedure described in the experimental section. The 90% confidence limits for the calibration curve in Fig. 2 correspond to deviations in  $Q_{\text{loss}}$  ranging from  $\pm 0.6\%$  to  $\pm 1.1\%$  for the 5 different calibration solutions. The average deviations in the measured values of  $\Delta T$  for the reacting solutions was  $\pm 0.3^\circ\text{C}$  which leads to an expected accuracy of the experimental volumetric heat capacities of  $\pm 3\%$ . Calculated results in Table 2 include the volumetric heat capacity without reaction, and for all but one bisulfite reaction, the volumetric heat capacity with reaction. The volumetric heat capacity without reaction is the weighted average of the pure component heat capacities (shown in Table 3) times the densities in Table 2. The value used for sodium bisulfite in solution was  $0.43 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$ . The volumetric heat capacity with reaction is the sum of the volumetric heat capacity without reaction and the contribution due to reaction. The contribution due to reaction is given by  $(\Delta H^0)(\Delta N_i)/\Delta T$ , where  $\Delta H^0$  is the heat of reaction in  $\text{cal mole}^{-1}$ ,  $\Delta T$  is the final temperature minus the initial temperature in  $^\circ\text{C}$ ,  $\Delta N_i$  is the change in moles per ml due to reaction when the change in  $T$  is  $\Delta T$ . Ref. 4 gives equilibrium constants at several temperatures for the first four bisulfite reactions. These data were used to calculate  $\Delta H^0$  and  $\Delta N_i$ . Values obtained for  $\Delta H^0$  were 8,400, 8,000, 10,600 and 8,200  $\text{cal g mole}^{-1}$ , respectively.

For all bisulfite additions, reaction contributed very little (less than 1%) to the

TABLE 3

Heat capacities used for pure reactants in calculations [9.10]

Component	Heat capacity (cal g <sup>-1</sup> °C <sup>-1</sup> )
Methyl ethyl ketone	0.541
Acetone	0.538
Ethyl acetoacetate	0.455
<i>n</i> -Butyraldehyde	0.507
<i>i</i> -Butyraldehyde	0.608
Methanol	0.601

solution heat capacity. The reason for this is that essentially all of the carbonyl compound is present as the bisulfite complex, even at the high temperature. The equilibrium constant for the complex formation is much greater than one.

Unlike the bisulfite reactions, the methanol–butyraldehyde solutions show a significant increase in the volumetric heat capacity due to reaction. For both normal and isobutyraldehyde the actual heat capacity is approximately twice that expected from the calculated value if no reaction occurred. The volumetric heat capacities in Table 2 under the heading “calculated with reaction” are also considerably less than the experimental values; they were calculated using equilibrium constants and heats of reactions from ref. 5. The ref. 5 data were measured in solutions dilute in the aldehyde. The higher experimental values are probably due to activity coefficient effects, or perhaps, increased heat effects due to the concentrated solutions. In any event it is encouraging from an energy storage viewpoint, that the actual heat capacities are higher, rather than lower, than the calculated values. This indicates that thermodynamic data at varying conditions are useful for screening reactions for energy storage purposes, but that for design purposes energy storage capacities should be determined experimentally. The methanol–butyraldehyde mixtures examined in this work are not likely to be used for energy storage because they do not have heat storage capacities greater than water. The results do indicate, however, that chemical reaction can significantly increase the energy storage capacities of liquid mixtures. It is likely that further work will identify reaction systems that employ this same mechanism to obtain energy storage capacities greater than water, and it seems likely that calorimetry will play an important role in this continuing work.

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