
01 Jan 1983

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Recommended Citation

B. G. Sparks and B. E. Poling, "Energy Storage Capacity Of Reversible Liquid-phase Diels Alder Reaction Between Maleic Anhydride And 2-methyl Furan," *AIChE Journal*, vol. 29, no. 4, pp. 534 - 537, Wiley; American Institute of Chemical Engineers (AIChE), Jan 1983.

The definitive version is available at <https://doi.org/10.1002/aic.690290403>

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Energy Storage Capacity of Reversible Liquid-Phase Diels Alder Reaction between Maleic Anhydride and 2-Methyl Furan

Calorimetry was used to determine the heat of reaction and equilibrium constant at 318 K for the reaction between maleic anhydride (*A*) and 2-methyl furan (*B*). The values were -60 kJ/gmol and 614 cm³/gmol, respectively. The motivation for this work was to find a single phase-reacting system that could be used to store solar energy. Thus, the energy storage capacity was calculated for a mixture of *A* and *B*, both initially at 7 kmol/m³, in dioxane. The maximum apparent heat capacity of 7.37 J/cm³·K occurred at 334 K. This maximum value is 76% higher than the heat capacity of pure water.

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SCOPE

Solar energy is frequently stored by heating water during the day and cooling it at night. It is often desirable to increase the amount of energy that can be stored in a given volume with minimal increase in the complexity of the storage system. One way to do this is to replace the water by chemicals which can react reversibly in the liquid phase. If this reaction occurs due to a change in the equilibrium composition with temperature, the mixture could potentially demonstrate an apparent heat capacity higher than that of water. This method of increasing the energy storage capacity would not require a phase change, but could be in addition to a phase change. Details of these concepts have been developed previously, comparisons to other storage methods have been made, and storage capacities for various hypothetical values of the heat of reaction and equilibrium constant have been calculated (Poling, 1979; Lenz and Hegedus, 1979; Poling et al., 1981).

It has been also shown that the heat capacity of a mixture can be increased due to chemical reaction (Mastroianni and Poling, 1982). Prior to this work, however, no chemical reaction was known which resulted in an apparent heat capacity higher than

that of water. Even though the concepts are straightforward, identification of reactions that give high energy storage capacities is difficult. Desired properties (equilibrium constants and heats of reaction) cannot be predicted. Equilibrium compositions are not easy to measure with common analysis techniques. For example, the product breaks down when subjected to gas chromatography and the solutions are too concentrated for spectrophotometric methods.

Thus, the objective of this paper was: first to identify a reaction mixture that possessed an apparent heat capacity (and thus energy storage capacity) greater than water; and second to measure this energy storage capacity. These objectives were accomplished by making isothermal calorimetric measurements to determine the heat of reaction and equilibrium constant at 318 K for the Diels Alder reaction between 2-methyl furan and maleic anhydride. These results were coupled with adiabatic heat capacity measurements for the pure components to calculate the energy storage capacity vs. temperature for a mixture with initial concentrations of both maleic anhydride and 2-methyl furan of 7 kmol/m³.

CONCLUSIONS AND SIGNIFICANCE

The two conclusions of this work are that the heat of reaction and equilibrium constant of a reversible reaction can be determined by calorimetry, and that a mixture of maleic anhydride (*A*) and 2-methyl furan (*B*) in dioxane has a maximum apparent heat capacity of 7.37 J/cm³·K (1.76 cal/cm³·K) at 334 K.

Isothermal calorimetry was used to measure the heat generated by reaction when *B* was injected into a solution of *A* in dioxane. A series of these runs at varying concentrations, all at 318 K, allowed determination of both the equilibrium constant and heat of reaction. These values were 60 kJ/gmol and 614

cm³/gmol, respectively.

The energy storage capacity was then calculated for a mixture of *A* and *B* in dioxane, both initially at 7 kmol/m³. The average apparent heat capacity for this mixture between 310 and 360 K was 6.92 J/cm³·K, a value 65% higher than that of water. This temperature range is typical for flat plate solar collectors. To date, this is the only homogeneous liquid-phase mixture demonstrated to have a volumetric heat capacity greater than that of water.

INTRODUCTION

Solar energy collected as heat by flat-plate solar collectors is usually stored by heating water during the day and cooling it at

night. The energy stored in a given volume can be increased if the water is replaced by materials which undergo a phase change. Another way to increase the energy storage capacity is to replace the water with chemicals which undergo a chemical reaction as the temperature in the storage vessel changes. This scheme does not require phase changes or separation of any of the reacting species.

Figure 1 illustrates what can happen to a reacting mixture as the

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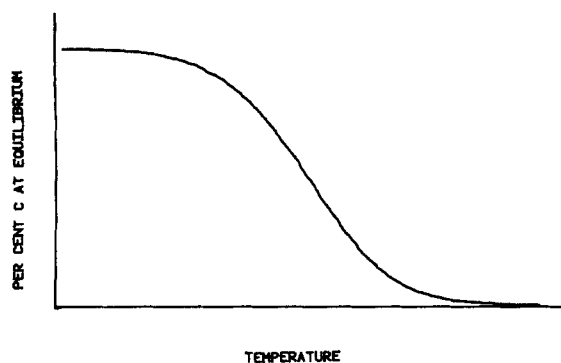


Figure 1. Per cent C at equilibrium vs. temperature in a mixture when the exothermic reaction, $A + B \rightleftharpoons C$ can occur. Reaction occurs because the temperature is changed.

temperature is changed. Figure 1 is for the exothermic reversible chemical reaction, $A + B \rightleftharpoons C$. To heat the mixture requires a certain amount of sensible heat. With this increase in T , some C will decompose to A and B , so the heat of reaction must also be supplied. When the mixture is cooled to the original temperature, the mixture will return to its original composition; both the sensible heat and heat of reaction will be recovered. Because the reaction occurs, the apparent heat capacity of the liquid solution will be greater than the sum of the pure component heat capacities.

For a reaction to provide a sufficient increase in the energy storage capacity, it must have a high heat of reaction, the right value for the equilibrium constant (neither too high nor too low) and require little or no solvent. It is difficult to identify reactions which possess these properties. The compound C must be rather unstable for the reaction to store energy. But if C is unstable, equilibrium compositions cannot be measured by conventional techniques such as gas chromatography. Thus, equilibrium constants and heats of reactions are not available for the many reactions which could conceivably possess properties desirable for energy storage. In this paper, we present a calorimetric technique for measuring equilibrium constants and heats of reaction for reversible reactions of the form $A + B \rightleftharpoons C$ when C decomposes rapidly as the temperature is increased.

Diels Alder reactions are a class of reactions which might be used for energy storage. Examples of Diels Alder reactions can be cited that are reversible and which have sufficiently high heats of reaction (Poling et al., 1981). Seltzer (1963) has reported an approximate value of 1.7 kmol/m^3 for the equilibrium constant for the reaction between 2-methyl furan and maleic anhydride. This value was obtained at 323 K with all the reacting species dilute in CCl_4 . We have used the previously mentioned calorimetric technique to measure the equilibrium constant for this reaction at higher concentrations more suitable for energy storage. The heat of reaction has also been determined. These values have been used to calculate an energy storage capacity, and the significance and limitations of these calculations are discussed.

EXPERIMENTAL AND RESULTS

Experiments were conducted in a Tronac Model 550 isothermal titration calorimeter. In each experiment, an accurately measured volume (less than 0.2 cm^3) of a 2-methyl furan (B) solution was injected into 25 cm^3 of a maleic anhydride (A) solution contained in a stainless-steel reaction vessel. The solvent was *p*-dioxane and the concentrations of A and B were the same in their respective solutions prior to injection. These concentrations ranged from 3.0 to 7.3 kmol/m^3 . Prior to injection, the bomb and methyl furan solution were immersed in a constant temperature bath held at 317.8 K . Temperature was measured to $\pm 0.05 \text{ K}$ and was controlled, in the bath to $\pm 0.0001 \text{ K}$. Maleic anhydride was obtained from Fisher; 2-methyl furan and *p*-dioxane were obtained from Aldrich. These chemicals were used without further purification.

After injection, the reaction, $A + B \rightleftharpoons C$, occurred at constant temperature. To maintain constant temperature, a thermopile removed heat from

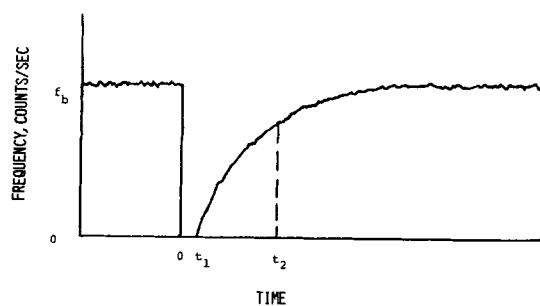


Figure 2. Typical heater frequency plot. Injection of 2-methyl furan solution occurred at time zero.

the reaction vessel at a constant rate, and at any instant heat supplied by the reaction plus heat supplied by a heater operating at a measured frequency, f , just balanced the cooling. Determination of K and ΔH_R actually required three steps. First, the frequency plot for a run was obtained. Second, the cumulative heat generated by reaction had to be determined by some appropriate procedure. Third, K and ΔH_R had to be determined from the results of a series of runs.

Figure 2 is typical of the frequency vs. time behavior for a single experiment and shows the four distinct time periods. Prior to injection at time zero, the heater operated at a baseline frequency, f_b . The second time period occurred just after injection. Here heat generation by reaction was at its highest value. For the case shown in Figure 2, the heat generated by reaction was so great that the heater did not operate between time zero and t_1 . During this period, the temperature in the bomb was actually greater than 45°C , and a heat leak correction had to be applied. To accomplish this, the difference in the bomb and bath temperatures was integrated between 0 and t_1 . This temperature difference, along with a heat leak coefficient determined separately by calibration allowed determination of Q_{HL} , the heat transferred during the nonisothermal period. Q_{HL} was typically 0.2% of the total heat generated by reaction, Q^∞ . During the third time period shown in Figure 2, between t_1 and t_2 , frequency was integrated with an automatic integrator. At t_2 , the automatic integrator was turned off and the last portion of the curve was obtained on a recorder. Thus, the cumulative heat generated by reaction at any time greater than t_2 was calculated by

$$Q = cf_b t - c \int_{t_1}^{t_2} f dt - c \int_{t_2}^t f dt + Q_{HL} \quad (1)$$

c is a constant, determined by a separate calibration experiment, to convert heater frequency to J/s .

There are three methods one could use to obtain Q^∞ from the Figure 2 information. The simplest method would be to pick t in Eq. 1 sufficiently large so that the reaction was at equilibrium. This method, however, is not good because the first and third terms on the right side of Eq. 1 become very large; small errors in these terms due for example to baseline drift lead to large errors in Q^∞ . A second method to obtain Q^∞ would be to use the fact that the reaction, and thus the curve in Figure 2 obeyed first-order kinetics (the initial concentration of maleic anhydride was about 250 times greater than that of methyl furan). Thus, one could fit the frequency vs. time data directly to the appropriate first-order equation. This method fails because the Figure 2 curve does not obey first-order kinetics at small times (the injection is not instantaneous). In the third method, which we used, several values of Q were determined by Eq. 1 at times greater than t_2 , and these were fit by nonlinear regression to the integrated first-order equation:

$$Q = Q^\infty (1 - e^{-kt}) \quad (2)$$

This technique, which avoided the uncertainties at both small and large times, gave values of Q^∞ with an estimated uncertainty of 1%.

The technique illustrated by Figure 2 (which is a variation on the procedure recommended in the operating manual) has been used previously for mixing processes (Nakamura et al., 1982). To our knowledge, the technique has not been used for reactions that do not occur instantaneously (the half life of this reaction was about three minutes).

The final step in the procedure was to determine K and ΔH_R from values of Q^∞ . Q^∞ is not equal to the heat of reaction because the reactions did not go to completion. Thus, a method was devised to determine both K and ΔH_R from the experiments just described. Activity coefficients were taken as unity. Thermodynamically, it is better to approximate the activity by the mole fraction rather than by concentration, but there is evidence that K_C , an equilibrium constant based on concentrations may be more nearly composition-independent than K_x , i.e., one based on mole fractions (Kuntz et al., 1968). In any event, we chose to use an equilibrium constant based

TABLE 1. EXPERIMENTAL RESULTS: HEAT EVOLVED BY REACTION TO EQUILIBRIUM AT 318 K AT DIFFERENT MALEIC ANHYDRIDE CONCENTRATIONS

Maleic Anhydride Concentration, C_{Ao} , kmol/m ³	2-Methyl Furan Added, N_{Bo} , gmol × 10 ⁴	Heat Evolved by Reaction, Q^∞ , J
3.0	2.88	11.17
4.0	8.08	34.56
5.0	4.45	20.18
6.0	6.72	31.71
7.3	7.52	36.59

TABLE 2. HEAT CAPACITIES FROM ADIABATIC CALORIMETER AT 298 K

	Heat Capacity J/g·K	Experimental Density g/cm ³
p-Dioxane	2.137	1.03
2-Methyl Furan	2.397	0.824
Maleic Anhydride Solution, 7 kmol/m ³ in Dioxane	1.792	1.20
Equilibrium Mixture* of Maleic Anhydride, 2-Methyl Furan, and Their Adduct	2.198	1.20

* The initial concentration of the maleic anhydride and 2-methyl furan was 4.88 kmol/m³.

on concentrations and assumed the concentration of maleic anhydride, C_{Ao} , remained constant. Thus,

$$K = \frac{C_C}{C_A C_B} = \frac{N_C}{C_{Ao}(N_{Bo} - N_C)} \quad (3)$$

Q^∞ was the heat of reaction, ΔH_R , times the moles of adduct, N_C , that were formed.

$$Q^\infty = (\Delta H_R)(N_C) \quad (4)$$

Eliminating N_C from Eqs. 3 and 4 gave

$$\frac{N_{Bo}}{Q^\infty} = \frac{1}{C_{Ao}K\Delta H_R} + \frac{1}{\Delta H_R} \quad (5)$$

A series of experiments were run with different values of C_{Ao} and the results are shown in Table 1. Equation 5 indicated a plot of N_{Bo}/Q^∞ vs. $1/C_{Ao}$ would be a straight line from which ΔH_R and K could be determined. Figure 3 is such a plot. The line is a least squares fit and gives values for ΔH_R and K of -60 kJ/gmol and 614 cm³/gmol, respectively. The regression coefficient was 0.996. These values of K and ΔH_R , along with the equation $d \ln K/dt = \Delta H_R/RT^2$, gave a K at 323 K of 426 cm³/gmol. This is surprisingly close to the value reported by Seltzer (1963) of 590 cm³/gmol, considering his value was for a much lower concentration of maleic anhydride and in CCl₄, rather than dioxane.

The energy storage capacity of a reaction mixture is the sum of the heat of reaction term and sensible heat term. To determine the sensible heat term, pure component heat capacities were determined at 298 K in an adiabatic calorimeter and with Eq. 6.

$$C_P = \frac{Q}{\Delta T} - C_{P,bomb} \quad (6)$$

Q was the heat supplied by the heater; ΔT was the resulting change in temperature; and $C_{P,bomb}$ was 22.27 J/K, as determined by calibration. The solution volume was 50 cm³. Results of these measurements are shown in Table 2. The experimental value for the equilibrium mixture was corrected for the small amount of reaction that occurred in the time required for the measurement (40 s). Values used to estimate this correction were 0.01 m³/kmol-min and 0.0036 min⁻¹ for the forward and reverse rate constants, and 48.6 and 108 kJ/gmol for the forward and reverse activation energies. Thus, the "sensible" heat capacity (with no reaction) was 2.164 rather than 2.198 . This led to heat capacities for maleic anhydride and adduct in solution of 1.792 and 1.687 J/g·K, respectively. These values then gave ΔC_P equal to -67 J/gmol·K.

Kinetic parameters were determined from the fact that the constant, k , in Eq. 2 is equal to the forward rate constant divided by the equilibrium conversion. Thus, the Figure 2 information allowed estimates of the forward and reverse rate constants at 45°C . The experiments used to generate Figure 3 were repeated at 25°C . Due to the increase in half life of the reaction,

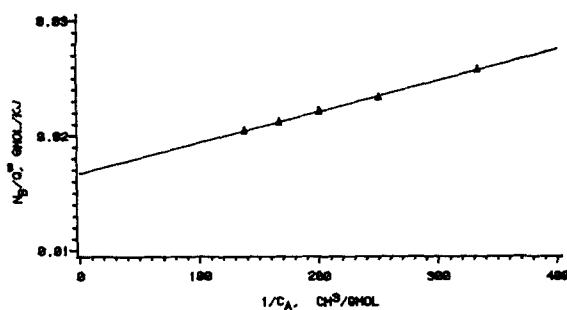


Figure 3. Plot of N_{Bo}/Q^∞ vs. $1/C_{Ao}$. The line is a least squares fit of the data

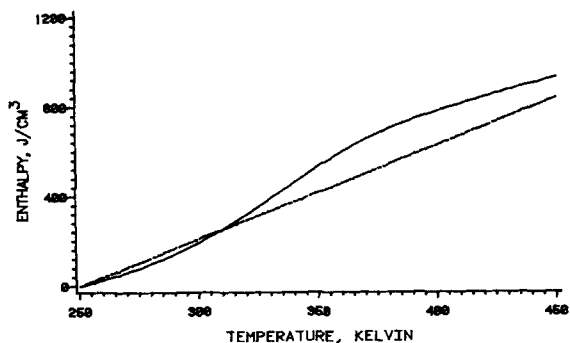


Figure 4. Enthalpy versus temperature for a mixture of maleic anhydride and 2-methyl furan both initially at 7 kmol/m³ in p-dioxane. The dotted line is for water and the reference T is 250 K.

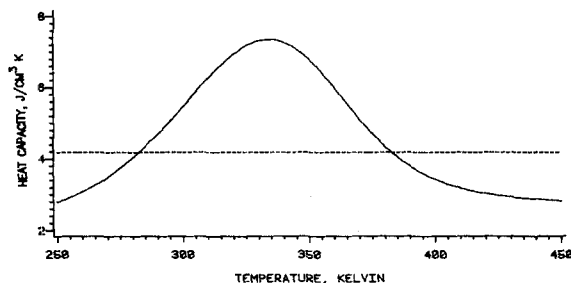


Figure 5. Heat capacity, J/cm³·K, vs. temperature for a mixture of maleic anhydride and 2-methyl furan, both initially at 7 kmol/m³ in p-dioxane. The dotted line is for water.

and corresponding reduction in accuracy, these experiments did not provide additional information about the equilibrium constant and heat of reaction; but they did allow estimates of rate constants at 25°C .

Figure 4 shows the volumetric enthalpy of a reaction mixture, initially 7 kmol/m³ in reactants, vs. temperature. The enthalpy of water is shown as a dotted line for comparison. The reference temperature is 250 K. The difference in enthalpy between any two temperatures is the amount of heat that would be stored for that temperature change. The equation used to generate Figure 4 is:

$$H = \underbrace{\int \left(\sum_i C_{pi} N_i \right) dT}_{\text{sensible heat}} - \underbrace{\int \Delta H_R dN_C}_{\text{heat due to reaction}} \quad (7)$$

The lower limit of integration is 250 K, so H is the heat required to heat the mixture from 250 K to the upper limit of integration, T . Pure component heat capacities, C_{pi} , and the heat of reaction, ΔH_R , are those values given previously that were determined by calorimetry. ΔH_R in J/gmol is given as a function of T by

$$\Delta H_R = -60,000 - 67(T - 318), \quad T \text{ in K} \quad (8)$$

N_i is the number of moles of component i per volume of equilibrium mixture and except for the solvent, is a function of T (Eq. 3); the summation is over all components in the mixture; and dN_C is the change in the moles of adduct per volume of mixture. The derivative of the curve in Figure 4 is shown in Figure 5. This derivative is the apparent volumetric heat ca-

capacity. A dotted line for water is shown for comparison. Below 250 and above 450 K, little or no reaction occurs and water has a higher energy storage capacity than the reaction mixture. Between 282 and 382 K, the heat capacity for the reaction mixture is higher than C_P for water because in this range, reaction occurs as the temperature changes. The maximum heat capacity is $7.37 \text{ J/cm}^3\cdot\text{K}$ at 334 K. Flat-plate solar collectors typically operate between 310 and 360 K; the average heat capacity over this range is $6.92 \text{ J/cm}^3\cdot\text{K}$, 65% higher than water.

Figures 4 and 5 are calculated results based on an initial concentration of maleic anhydride and 2-methyl furan in p-dioxane of 7 kmol/m^3 . High concentrations of reacting species are necessary for a high energy storage capacity; a solution with both species at 7 kmol/m^3 was prepared to insure that these concentrations were possible. Below about 305 K, precipitation occurred so that a concentration of 7 kmol/m^3 was no longer possible. Thus, points below 305 K on Figures 4 and 5 are for a hypothetical liquid state that would not exist. The true energy storage capacity would be increased by the heat of fusion of the precipitate. An energy storage scheme which incorporated this phase change would have an energy storage capacity two to three times that of water, though it would be more complex.

The estimated uncertainty in the Figure 5 results is about 5%. This uncertainty arises for several reasons. First, the equilibrium constant was determined experimentally when 2-methyl furan was dilute; Figure 5 is calculated for a high methyl furan concentration. The assumption that the methyl furan activity coefficient is constant over the large composition change may not be valid. If this activity coefficient were not constant, this would shift the temperature where the maximum heat capacity occurred, but would not change the value of the heat capacity. The adduct heat capacity and ΔC_P are rather uncertain with estimated uncertainties of 10 and 25% respectively. These quantities have only a small effect on the Figure 5 results. Heat capacities in Figure 5 have been reported as volumetric heat capacities because this quantity is of more interest in sizing energy storage systems. Densities at 298 K were used to convert mass heat capacities to volume heat capacities. However, the volume change on reaction for a Diels Alder reaction can be as much as 20% when pure reactants go completely to product. This effect, which would lower the values in Figure 5 at higher temperatures, was not included.

The uncertainties mentioned do not alter the conclusion that the energy storage capacity of the methyl furan–maleic anhydride reaction is significantly greater than that of water over the temperature range of 282 to 382 K. That such behavior is possible with at least one reaction implies that other reactions may exist which exhibit even higher energy storage capacities. The experimental techniques described in this paper will prove useful in determining these energy storage capacities.

Finally, we are not necessarily advocating that the methyl furan–maleic anhydride reaction be adopted for energy storage. Before adoption, a reaction must be evaluated in terms of its toxicity, flammability, and stability. It will be essential that those reactions, and reaction conditions which lead to irreversible side reactions be avoided. A general economic evaluation is difficult because one can conceive of many different applications. However, for an active solar energy system, preliminary estimates indicate that the break even point for storage by reaction instead of water might be when the heat capacity for the reaction mixture is approximately twice that of water (Mastroianni, 1979).

ACKNOWLEDGMENT

This work was done with the support of the U.S. Department of Energy, Grant No. EW-79-G-47-1026. However, any opinions, findings, conclusions or recommendations expressed herein are

those of the authors and do not necessarily reflect the views of DOE.

The authors wish to acknowledge G. L. Bertrand, Dept. of Chemistry, UMR, for this assistance with the calorimetric measurements.

NOTATION

c	= constant
C	= concentration
C_P	= heat capacity
$C_{P,\text{bomb}}$	= heat capacity of bomb, J/K
f	= heater frequency
H	= enthalpy, J/cm ³
ΔH_R	= heat of reaction, kJ/gmol
k	= constant
K_C, K	= equilibrium constant, based on molarity, cm ³ /gmol
K_x	= equilibrium constant based on mole fractions
Q	= cumulative heat evolved by reaction at any time, J
Q^∞	= cumulative heat evolved when reaction has reached equilibrium, J
Q_{HL}	= heat leak correction to Q^∞ , J
N	= mol or mol/volume
t	= time, min
T	= temperature, K

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Manuscript received February 4, 1982; revision received July 6, and accepted August 26, 1982.