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Estimation of Heat and Rate Constant of Reaction by a High-Speed Isothermal Calorimeter

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Abstract

An high-speed isothermal calorimeter which can trace the progress of a liquid phase reversible reaction was constructed using analog and digital computer. By means of a set point change of the calorimeter, the thermal energy capacity and the heat of reaction in reversible reaction mixture can be measured. The heat of reaction between 2-methyl furan and maleic anhydride and the heat capacities of the adduct were 61,200 J/mol and 2.38 J/ g K, respectively. Also reaction equilibrium constant and reaction rate constants can be estimated from the response curves of the calorimeter.

1. Introduction

Most chemical and physical processes are accompanied by heat effects. Because these heat effects may contain significant information concerning the mechanism of the process, the observation of the heat effects may be used to analyze the processes. Calorimetry is one of the most important methods for measuring heat effects.

Especially, chemical reactions are accompanied by the release or the absorption of energy in the heat form. The heat of reaction is definite and reproducible characteristic of a given chemical change. Also, the rates of chemical reactions are widely differentiated depending on reactants, temperatures, pressures etc. The characteristic time variation of the reaction rate is referred to as reaction kinetics. Therefore, the measurement of reaction heat and reaction kinetics is fundamental part of chemical process industry. These thermodynamic and kinetic parameters, such as the heat of reaction and the reaction rate constant, are obtained by analyzing data measured from calorimeter.

Isothermal calorimetry is based on measuring the energy required to maintain the reaction at a constant temperature during the course of a reaction. This condition is achieved in the calorimeter described here by adjusting the energy output of a controlled heater to balance the energy arising from the chemical reaction plus the energy removed by a cooler. This method is equally applicable to both endothermic and exothermic reactions.

However, various energy storage schemes involving reactions have been proposed but often involve higher temperatures and a vapor phase.[1,2] Such schemes have extensive equipment requirements such as pumps, heat exchangers, compressors, and storage vessels, etc. But the complexity of these systems renders them unsuitable for small scale applications. If reversible reactions took place and if all species were liquid, the heat storage scheme could escape from the restriction of higher temperature and extensive equipments. Reversible liquid-phase reactions may be attractive for energy storage scheme[3] because heat can be stored as a heat of reaction, as well as sensible heat, and these systems are capable of storing more heat than water. Therefore, reversibly reacting mixture have relatively higher heat storage capacity than their apparent specific heat. But these applications have been hindered by the lack of data.[4] The isothermal calorimetric technique has been presented data related to energy storage scheme used to reversible chemical reactants and/or products. Particularly, the isothermal calorimeter measurements may be applied to determine the heat of reaction and the equilibrium constant of reversible reaction.

In this work, a new high-speed isothermal reaction calorimeter is described that has been developed to study the heat storage capacity of reversible liquid-phase reactants

and/or products on a laboratory scale. The thermodynamic and kinetic parameters of the reversible reaction, such as the heat of reaction, the equilibrium constant of reaction, the heat storage capacity and the rate constant, are determined by isothermal calorimetric method with high accuracy and quick response.

2. Experimental Apparatus

The isothermal calorimeter consists of a 0.1 *l* stirred tank vessel. The schematic block diagram of the calorimeter is represented in Figure 2.1. The vessel is equipped with the

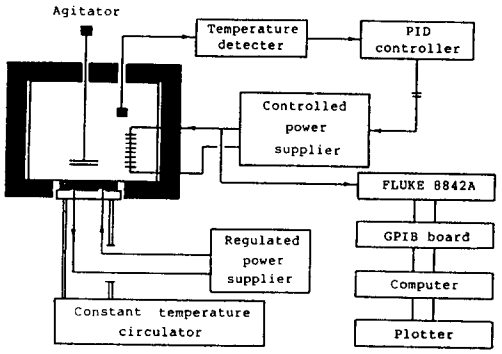

Fig 2.1 Schematic block diagram of experimental apparatus.

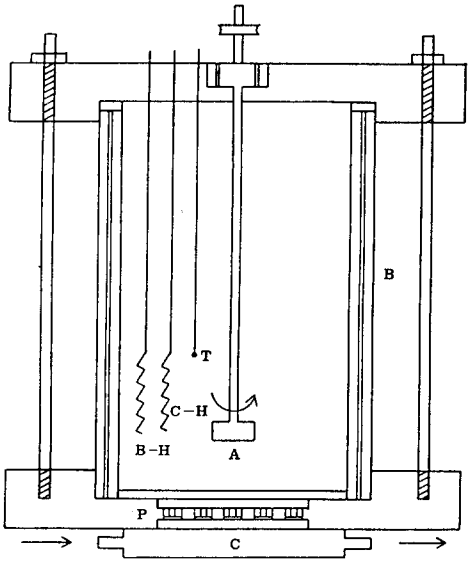

Fig 2.2 Detailed sketch of reacting vessel.
A: Agitator, T: Thermistor, B: Evacuated glass tube, C-H:Control heating element, B-H: Base heating element, P: Peltier cooling element, C: Cooling water heat sink

thermistor, the heater, and the cooler shown in Figure 2.2. The heater is consisted of two resistance heaters one for calibration purposes and one for adding electric energy to offset cooling. For high-speed calibration response, the power controllable heater is operated by electric signal which an analog computer with PID controller supply. In order to remove the heat constantly, the constant thermoelectric cooler (Peltier cooler) is operated by a constant current power supplier and the heat is removed by cooling water of thermostatic bath. Data acquisition is provided by an IBM PC. The controllable heater is interfaced with computer through A/D (analog and digital) interface board. The electric voltage data of the controllable heater is monitored and stored in PC and this data is used to analyze the results later.

3. Experimental Procedure

The calorimeter is operated by filling the reaction vessel with reactants and solvent. The contents of the calorimeter are brought to the set temperature by either cooling with Peltier cooler or heating with the heater. The electronic controls of the calorimeter are then set into operation. Adjusting the isothermal control unit to the maintain the reaction vessel at the set temperature. The equipment is then allowed to attain a steady state of operation. It takes approximately 1 hour, depending upon the starting temperature of the solution and calorimeter, for the entire system to reach optimum control. At this point, a set point changes in the calorimeter. A/D converted signal of the control heater voltage change supplied into the calorimeter is monitored in PC. In order to increase the temperature of the set point changes in reactants, the recorded voltage signal was converted electric current of the controllable heater, and this current was integrated for the time until another steady state was obtained.

4. Theoretical

Consider a single liquid phase reaction

$$\sum_{j=1}^{N} \nu_j A_j = 0 \qquad (1)$$

occurring in solvent. Here A_j stands for chemical species and ν_j for the corresponding stoichiometric coefficient with the usual notation that $j=1,2,\ldots,M$ for products, $j=M+1, M+2, \ldots, N-1$ for reactants, and $j=N$ for solvent. The

energy storage capacity is defined the quantity of the heat per unit volume per unit temperature(1 K). For given temperature change dT, the change of the extent of reaction, $d\xi$, was varied and the energy storage capacity in these reaction mixture is described as follows

$$vC_E = \Sigma\, n_j Cp_j + \Delta H \frac{d\xi}{dT} \qquad (2)$$

where

$$\Delta H = (\Delta H^R + \Delta H^E) = \Sigma\, \nu_j\, (H_j + H_j^E) \qquad (3)$$

$$d\xi = \frac{dn_j}{\nu_j} \qquad (4)$$

ξ is designated the extent of the reaction. ΔH above is the sum of the heat of reaction and the heat of mixing and considered the heat of mixing which is corresponded the change of the extent of the reaction, $d\xi$. The number of moles of species j, n_j, is described by the extent of the reaction, ξ, and the derivative of the equilibrium constant K for the temperature obeying van't Hoff's isochore yields as follow

$$R\,T^2 \frac{d\xi}{dT} = \frac{\Delta H}{(\partial \ln K / \partial \xi)} \qquad (5)$$

where

$$\frac{\partial \ln K}{\partial \xi} = \Sigma \frac{\nu_j}{n_{oj} + \nu_j\, \xi} + \frac{\nu}{n_o + \nu\, \xi} \qquad (6)$$

$$\nu = \Sigma\, \nu_j$$

Therefore, the energy storage capacity in this reaction mixture defined in Eq. (2) yields Eq. (7) described as the function of the extent of the reaction and the temperature.

$$vC_E = \Sigma\, n_{oj}\, Cp_j + \Delta Cp\, \xi + \frac{(\Delta H)^2}{R\,T^2} \frac{\partial \xi}{\partial \ln K} \qquad (7)$$

If the extent of the reaction were determined using the method of proposed Thompson et al.[5], and if the heat capacities of reactants and products were measured already, the summation of the heat of reaction and the heat of mixing, ΔH, would be obtained with the energy storage capacity, C_E. As ΔH is due to infinitesimal temperature change dT, the heat of reaction is relatively less than the heat of reaction, ΔH is the regarded as the heat of reaction. This method has the high precision compared to conventional method which added each reactants respectively. As the products of the reversible reaction are decomposed to the reactants, it is impossible to measure the specific heat of products. Therefore, Eq.(7) can be rearranged to classify into reactants and products as follows:

$$vC_E = \Sigma(n_{oj} + \nu_j\, \xi)Cp_j + \Sigma(n_{oi} + \nu_i\, \xi)Cp_i + \frac{(\Delta H)^2}{R\,T^2} \frac{\partial \xi}{\partial \ln K} \qquad (8)$$

i, for reactants, j, for products

In Eq. (8), unknown variables, such as the heat capacities of the products and the heat of reaction, are remained. If the heat capacities of the products were independent upon the temperature and if ΔH were proportional to the temperature linearly, Eq. (8) could be arranged as follows:

$$vC_E = \Sigma(n_{oj} + \nu_j\, \xi)Cp_j + \Sigma(n_{oi} + \nu_i\, \xi)Cp_i + \frac{(a + bT)^2}{R\,T^2} \frac{\partial \xi}{\partial \ln K} \qquad (9)$$

i, for reactants, j, for products

If Eq. (9) were applied data from data varied temperature, the heat capacities of the reactant and the products could be determined by the regression analysis method. For any elementary reaction, $A_1 = A_2$, in the solvent, A_3, the unknown variables, the heat capacities of the reactant and the product, such as Cp_1, Cp_2, Cp_3, are determined for the regression analysis. As Cp_i and Cp_j are linear respectively and ΔH is nonlinear in Eq. (9), this regression analysis are easily solved using Newton's iteration method.

5. Results and Discussion

The vessel is filled with 70 mL of pure water and the supplied voltage change is measured in order to determine the vessel's heat capacity of the calorimeter. One typical example of the supplied voltage change measured at 298 K is shown in Figure 5.1. This figure shows a result that the switch is operated to return the previous temperature of steady state after the set point change. Results of measurements of the pure water are used to determine the

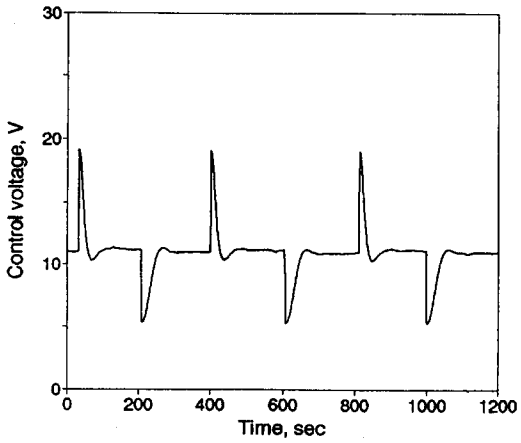

Fig 5.1 0.1 K set point change response voltage of calorimeter for water at 298 K.

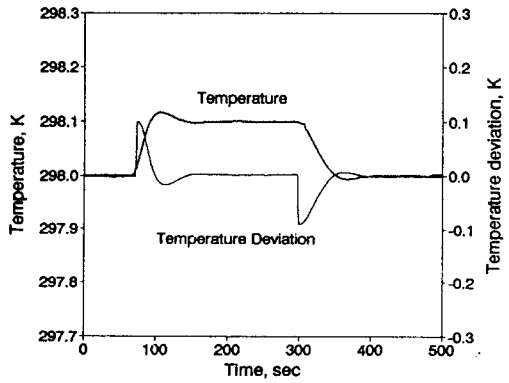

Fig 5.3 Response of calorimeter temperature for 0.1K set point change of water at 298K and its deviation from the set point.

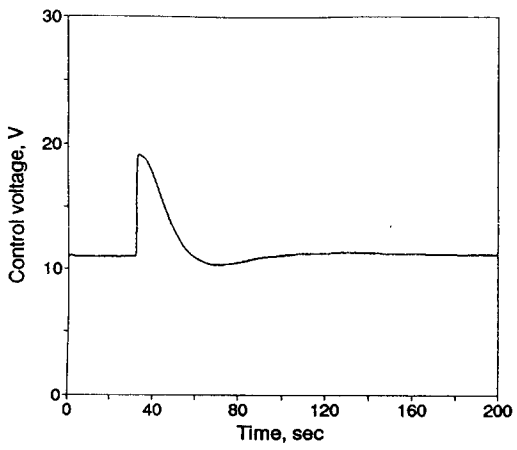

Fig 5.2 Magnified set point change response voltage of calorimeter for water at 298 K.

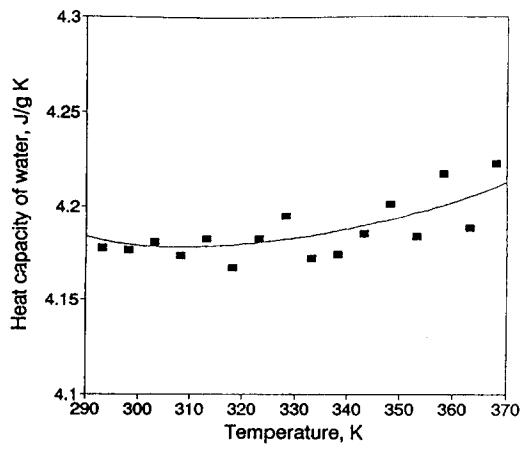

Fig 5.4 Comparison of the heat capacity of water with literature.

vessel's heat capacity at various temperature. Average area of the repeated experiments is converted into the power consumption to increase temperature 0.1 K of the pure water and the vessel. Figure 5.2 shows the first peak magnified in Figure 5.1, which is infinitesimally oscillating at steady state. Therefore, the heat loss of the vessel and cooling rate are negligible due to the set point change, 0.1 K. Figure 5.3 shows the response of the temperature and temperature deviation in the vessel of calorimeter. This shows that the response of the temperature is instantly stabilized after a little overshooting. The deviation between the temperature of set point and one of vessel was quickly stabilized within 1/1000 K compared to steady state. The heat capacities of the water was shown Figure 5.4,which is good agreement with the value of reported reference [6]. The accuracy in these runs is determined to be about 3%.

Energy storage capacities of the reactant and/or products with reversible chemical reaction between maleic anhydride and 2-methyl furan in 1,4-dioxane are measured. The initial mole fraction of both maleic anhydride and 2-methyl furan was 0.240. The vessel was filled with these reactant and solvent, 70 mL. Figure 5.5 shows the curve in response to voltage supplied at 298 K. This figure is that the longer time reaching the steady state and the smoother the shape of peak compared to Figure 5.2. These results show that 0.1 K change is slowly proceeded due to endothermic reaction and

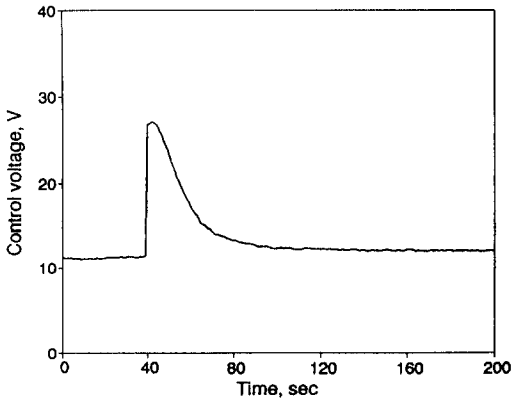

Fig 5.5 Response of calorimeter for the reaction of 2-methyl furan with maleic anhydride in p-dioxane at 298 K. Initial mole fraction of the reactant and the solvent was 0.24 and 0.520, respectively.

the heat is supplied continuously. Figure 5.6 shows the heat of reaction observed within the temperature ranges from 298 K to 368 K. The heat of reaction is higher than the data proposed Sparks and Poling [7]. This result shows that the value is 61,200 J/mol at 318 K in this work compared to the value of Sparks and Poling, 60,000 J/mol.

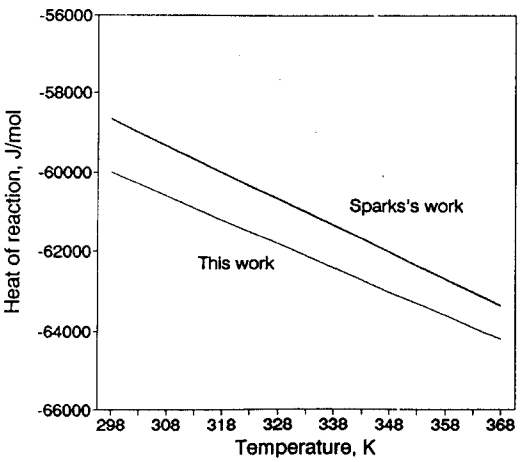

Fig 5.6 Heat reaction as a function of temperature.

Figure 5.7 shows the equilibrium constant of the reversible reaction between maleic anhydride and 2-methyl furan. Figure 5.8 shows the energy storage capacities varied temperature concentrations and varied initial concentration. BEcause forward and reverse activation energy and rate constant of this reaction is calculated from the computer

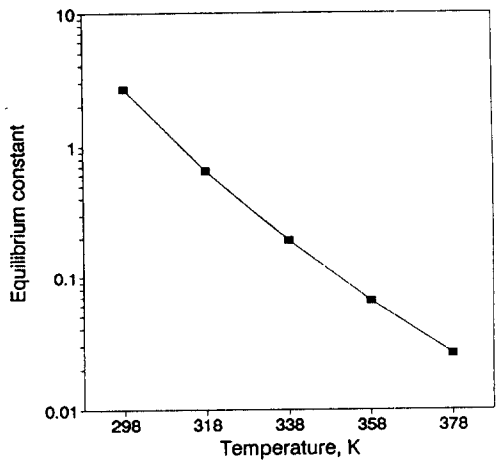

Fig 5.7 Dependence of reaction equilibrium constant on temperature.

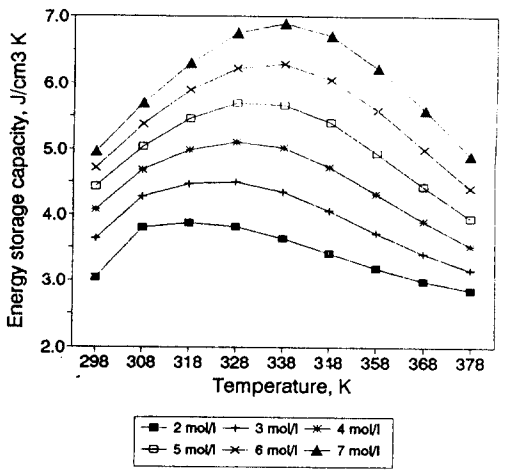

Fig 5.8 Effect of temperature and concentration on the heat storage capacity of various initial concentrations of maleic anhydride and 2-methyl furan.

simulation of this calorimeter, the activation energy of forward reaction at 318K is 48.6 kJ/mol and the forward rate constant is 0.00133 m^3/mol sec. The reverse activation energy and the reverse reaction constant are obtained from the relations of the equilibrium constant and the heat of reaction.

6. Conclusion

The isothermal calorimetric technique has provided the information concerning the thermodynamic and the kinetic of reactions under realistic conditions. Also the energy storage

capacities in reversible reaction are provided. These information can be used in many areas, such as identification of physical and chemical data, process development of energy storage scheme and process optimization. If the sophisticated isothermal calorimetry were studied, various information could be obtained measured from calorimeter.

Nomenclature

A_j	:	j-the chemical species [-]
C_E	:	thermal energy storage capacity [J/cm3 K]
Cp_i	:	heat capacity of species i [J/mol K]
ΔCp	:	$\Sigma\ \nu_j\ Cp_j$ [J/mol K]
Hi	:	enthalpy of species i [J/mol]
Hi	:	partial molar enthalpy of species i in mixture [J/mol]
ΔH	:	total enthalpy change [J]
ΔH^R	:	heat of reaction [J]
ΔH^E	:	heat of mixing [J]
K	:	equilibrium constant
n_j	:	number of moles of species j [mol]
T	:	temperature [K]
v	:	volume of reaction mixture [cm^3]
ν	:	$\Sigma\ \nu_j$ [-]
ν_j	:	stoichiometric coefficient for species j [-]
ξ	:	reaction coordinate [-]

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