Thermodynamic calculation

Oxidative carbonylation of ethanol and hydrolysis of diethyl ether were reaction (1) and reaction (2), respectively. The reaction (3) denoted the coupling reaction. The $\Delta_f H_m^\theta$, $\Delta_r S_m^\theta$, $\Delta_r G_m^\theta$ and $\Delta_r C_{p,m}$ of reaction (1)~(3) were shown in Table 1. From Table 1，reaction (1) and (2) were exothermic reaction and endothermic reaction, respectively. So both reactions could realize coupling of the energy. In the reaction (2), $\Delta_r G_m^\theta \rangle 0$, which indicates that hydrolysis of diethyl ether is not a spontaneous reaction in the standard state. Therefore, the calculation of relation between $\Delta_r G_m^\theta$ and temperature is necessary in the next succession. The $\Delta_r H_m^\theta$ of reaction (3) is 285.64KJ/mol, which makes clear that the coupling reaction is exothermic reaction. Enhancing the reaction temperature would go against producing of the objective product DEC. So controlling the reaction temperature of the coupling reaction is important for improving the reaction performance.

Table 1 The $\Delta_f H_m^\theta$, $\Delta_r S_m^\theta$, $\Delta_r G_m^\theta$ and $\Delta_r C_{p,m}$ of reaction (1)~(3).

	$\Delta_r H_m^\theta$ KJ/mol	$\Delta_r S_m^\theta$ J/(mol·K)	$\Delta_r G_m^\theta$ KJ/mol	$\Delta_r C_{p,m} = \Delta A + \Delta BT + \Delta CT^2$		
				ΔA	$\Delta B \times 10^3$	$\Delta C \times 10^6$
Reaction（1）	-309.47	-208.01	-247.45	-20.51	128.015	-119.325
Reaction（2）	23.83	33.79	13.75	-37.32	94.09	-66.95
Reaction（3）	-285.64	-174.22	-233.70	-57.83	222.105	-186.275

The standard enthalpy ($\Delta_r H_m^\theta$) of the reactions

The standard enthalpy ($\Delta_r H_m^\theta$) can be calculated using following equation:

$$\Delta_r H_m^\theta = \int \Delta_r C_{p,m} dT + H_0 \tag{4}$$

Which was based on Kirhhoff law（$\delta \Delta_r H / \delta T$）$_p = \Delta C_p$ and where H_0 is the integral constant.

The relationships between enthalpy change and temperature of these reactions were given in Fig. 1. As shown in Fig. 1, both the quantity of heat-producing during reaction (1) and that of heat-absorbing of reaction (2) descended gradually with temperature increasing between 300K and

700K. The extent of declining of both reactions was not too large, which could realize energy coupling of reaction. And that, the coupling reaction (3) from reaction (1) and (2) was an exothermal reaction. The quantity of heat-producing decreased gradually with temperature increasing.
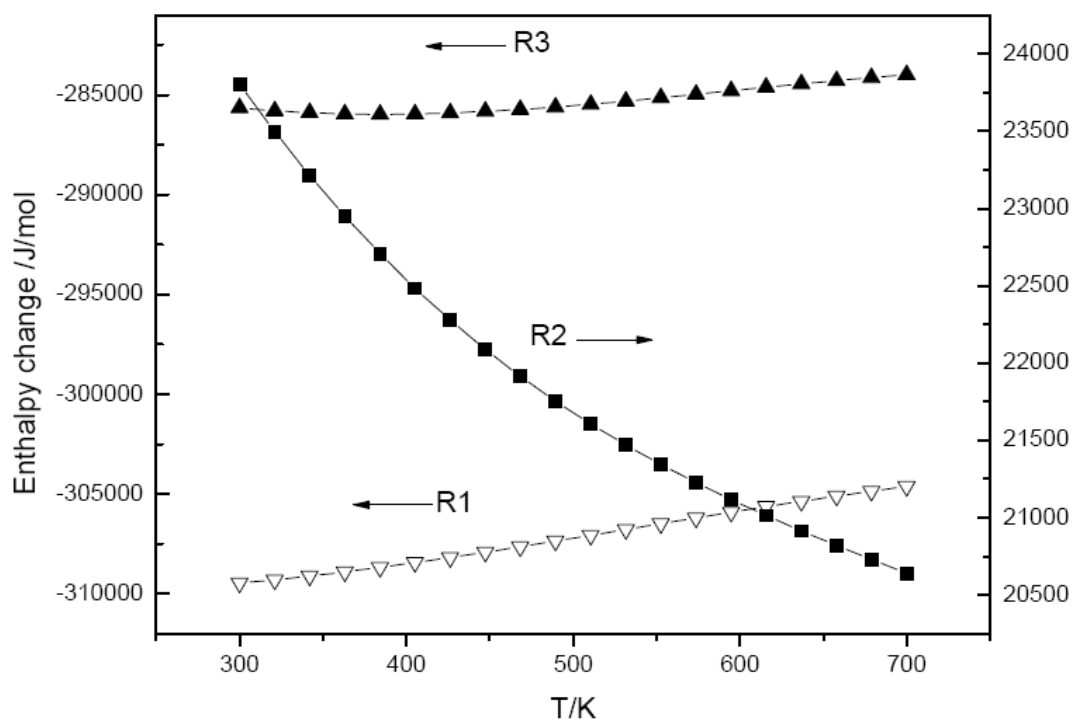

Fig. 1. Enthalpy change vs temperature.

The Gibbs free energy $\Delta_r G_m^\theta$

The Gibbs free energy ($\Delta_r G_m^\theta$) can be calculated using following equation (Gibbs-Helmholtz Equation), where I_0 is the integral constant.

$$\frac{\Delta G}{T} = -\int \frac{\Delta H}{T^2} dT + I_0$$

The De Donder [1] criterion of coupling reaction was shown in the following expressions:

$A_1 \cdot r_1 > 0$, $A_2 \cdot r_2 < 0$ and $A_1 \cdot r_1 + A_2 \cdot r_2 \geq 0$

Where A and r denote reaction affinity and reaction speed, respectively, and the suffix 1 and

2 mean the reaction (1) and (2). Under the constant temperature and equal pressure, the reaction

affinity (A) was equal to -ΔG. So the criterion was described in the expression:

$(\Delta G_1)_{T,P} \cdot r_1 < 0$, $(\Delta G_2)_{T,P} \cdot r_2 > 0$ and $(\Delta G_1)_{T,P} \cdot r_1 + (\Delta G_2)_{T,P} \cdot r_2 \leq 0$

From the expression, $(\Delta G_2)_{T,P}$ and r_2 was both positive or negative together. Therefore, the

thermodynamics trend of reaction (2) was opposite with the dynamics direction. The reaction (2)

does not progress spontaneously if the reaction is existed by oneself. But if the reaction (2) and

reaction (1) coexist, the reaction (2) is driven under $|(\Delta G_1)_{T,P} \cdot r_1| \geq |(\Delta G_2)_{T,P} \cdot r_2|$.
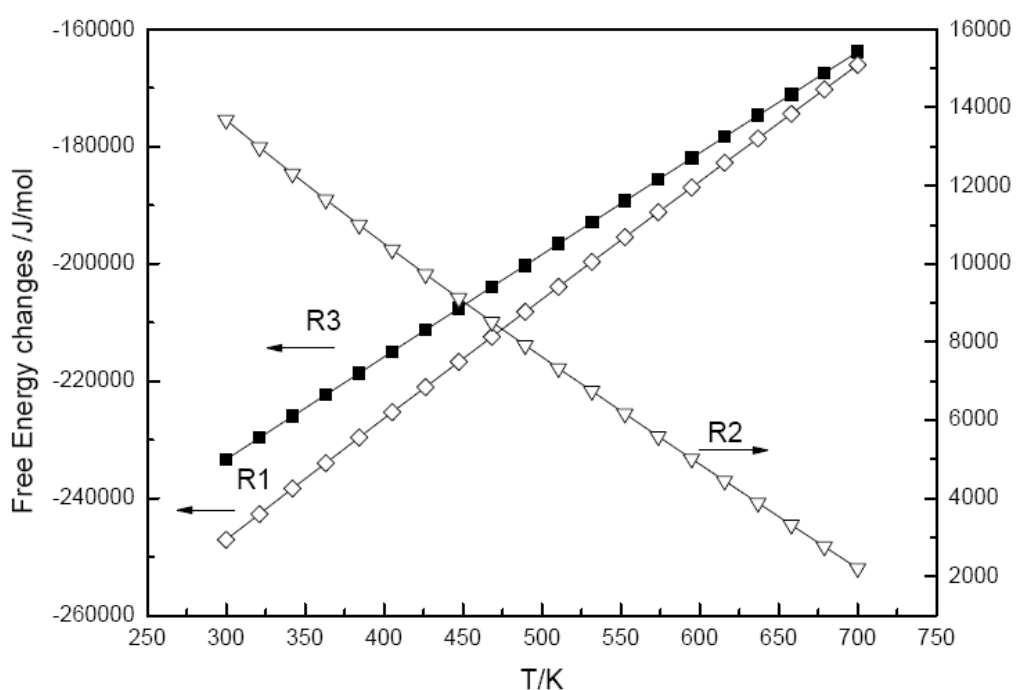

Fig. 2. Free energy changes vs temperature.

The relationship of free energy changes vs temperature was given in Fig. 2. As shown in Fig.

2, the free energy of reaction (3) was less than zero, which explained that the method of synthesis

of DEC with ethanol and diethyl ether together feeding was feasible on basis of thermodynamics.

In order to make reaction (2) proceed in the low temperature, both reaction (1) and (2) must satisfy

the expression $|(\Delta G_1)_{T,P} \cdot r_1| \geq |(\Delta G_2)_{T,P} \cdot r_2|$, which is $r_1/r_2 \geq |(\Delta G_2)_{T,P}/(\Delta G_1)_{T,P}|$. However, on

the other hand, the objective of diethyl ether introducing into the reactants is to eliminate or reduce the influence of the by-product water. The capacity of water-producing from reaction (1) is more than that of water-reacting in reaction (2). So in the mean time, the influence of water on the performance of catalyst was still existed. In a word, there was an optimal value of r_1/r_2 in the design of the coupling reaction.

Reaction equilibrium constants (K)

The reaction equilibrium constants (K) can be calculated using following equation:

$$\Delta_r G_m^{\theta} = -RT\ln K$$

The relationship of equilibrium constants vs temperature was given in Fig. 3. From Fig. 3, the equilibrium constants of reaction (1) and (3) decreased rapidly with temperature increasing. Though the equilibrium constant of reaction (2) increased with temperature increasing, the value of increasing was less than that of reaction (1).
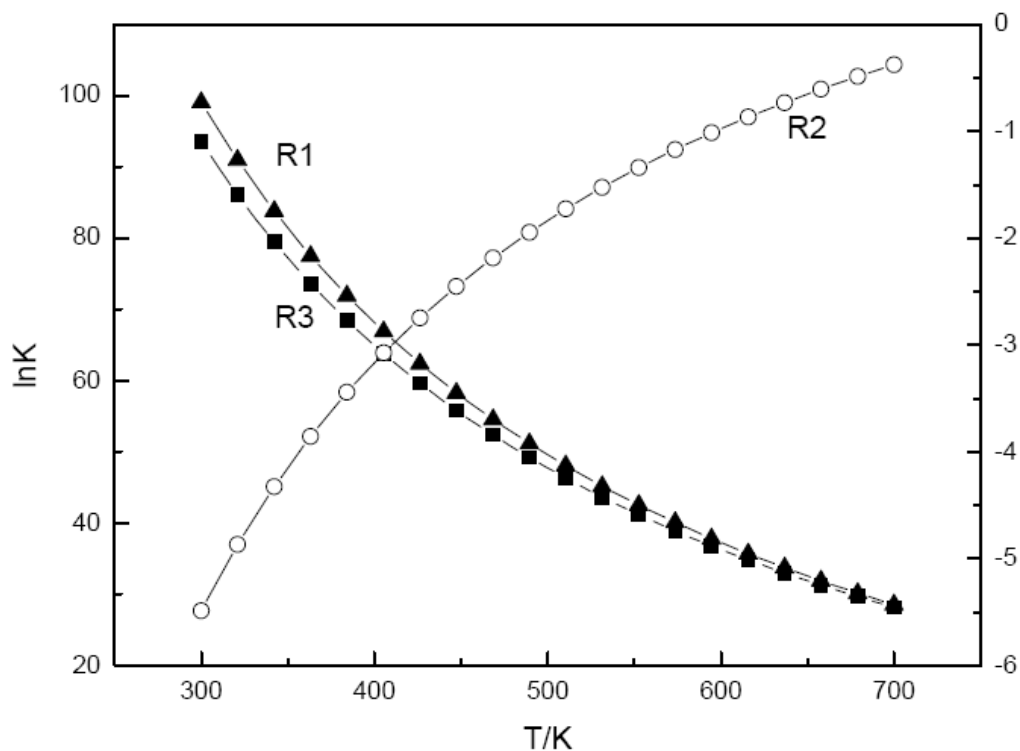

Fig. 3. Equilibrium constants vs temperature.

From the above analysis, in the range of certain temperature, reaction (1) and (2) were exothermic reaction and endothermic reaction, respectively. It could satisfy the energy coupling for reaction (1) and (2). In addition, the free energy of coupling reaction (3) was less than zero, which meaned that the design of coupling experiments was reasonable and the coupling reaction could be realized.

[1] I. Prigogine, R. Defay, *Chemical Thermodynamics, London: Longmans Green*, 1954, pp. 38–42, 262.