หอสมุดกลาง สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER 3

THERMODYNAMICS OF REACTIONS

3.1 Determination of the equilibrium constant

The dehydrogenation of ethylbenzene to styrene has simple reaction form as follows

$$C_6H_5CH_2{:}CH_3 \rightleftharpoons C_6H_5CH{:}CH_2 + H_2 \qquad H_{295}(R)=28100 \text{ cal}$$

In industry, this reaction occurs at temperature between 550-650°C. The equilibrium constant of this reaction is

$$K_p = \frac{P_s . P_{H_2}}{P_E} \qquad (1)$$

where K_p = equilibrium constant

P_s, P_{H_2}, P_E = partial pressure of styrene, hydrogen, ethylbenzene respectively

The equilibrium constant relative to temperature is

$$\ln K_p = \frac{-\Delta G_T(R)}{RT} \qquad (2)$$

where $\Delta G_T(R)$ = change in Gibb free energy due to reaction

R = gas constant

T = tempreature in Kelvin

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The value of $\Delta G_T(R)$ can be obtained from

$$\Delta G_T(R) = \Delta H_T(R) - T\Delta S_T(R) \qquad (3)$$

where $\Delta H_T(R)$ = change of enthalpy due to reaction

$\Delta S_T(R)$ = change of entropy due to reaction

The value of $\Delta H_T(R)$ can be determined as

$$\Delta H_T(R) = \Delta H_{298}(R) + \int_{298}^{T} \Delta C_p(R)dT \qquad (4)$$

where ΔC_p = change of heat capacity due to reaction

= ΔC_p (product) - ΔC_p (reactant)

The value of $S_T(R)$ can be obtained from

$$\Delta S_T(R) = \Delta S_{298}(R) + \int_{298}^{T} \frac{\Delta C_p(R)dT}{T} \qquad (5)$$

The values of thermodynamic are shown as follows

Table 3-1

	$\Delta H_{298}(R)$ cal/mole	$\Delta S_{298}(R)$ cal/mole	$\Delta G_{298}(R)$ cal/mole
Ethylbenzene	7,120		31,208
Styrene	35,220	27.5288	51,100
Hydrogen			

The heat capacity can be expressed in the terms of

$$C_p = a + bT + cT^2 + dT^3 \qquad (6)$$

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where a,b,c,d = constant

T = temperature in Kelvin

C_p = heat capacity in cal/mole.K

The value of the constants are show in table 3.2

Table 3.2(12)

The value of the constant

Substance	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^9$
Ethylbenzene	-8.398	15.935	-10.003	23.95
Styrene	-5.968	14.354	-9.150	22.03
Hydrogen	6.952	0.04576	0.09563	-0.2079

The values of the constants are in range $273 < T < 1500$ K

$$C_p(R) = C_p(H_2) + C_p(S) - C_p(E) \qquad (7)$$

Thus, from equations (3), (4), (5), (6), (7), table3.1, table3.2 we can calculate the change of Gibb free energy of the reaction. Using equation (2), knowing the value of Gibb free energy, the gas constant and the reaction temperature, we can calculate the equilibrium constant. The example of the calculation is shown in appendix C

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Table 3.3

The calculation data

T (K)	$\Delta G_T(R)$ (cal)	ln K_p	K_p
500	14,070.7	-14.1628	7.066×10^{-7}
600	11,062.7	-9.2792	9.33×10^{-5}
700	8,011	-5.7596	3.1524×10^{-3}
800	4,931.6	-3.1024	4.49×10^{-2}
900	1,834.9	-1.0261	0.3584
1000	-1,271.5	0.6399	1.8963
1100	-4,382.8	2.0052	7.4278
1200	-7,495.4	3.1435	23.1851
1300	-10,604.3	4.1053	60.653

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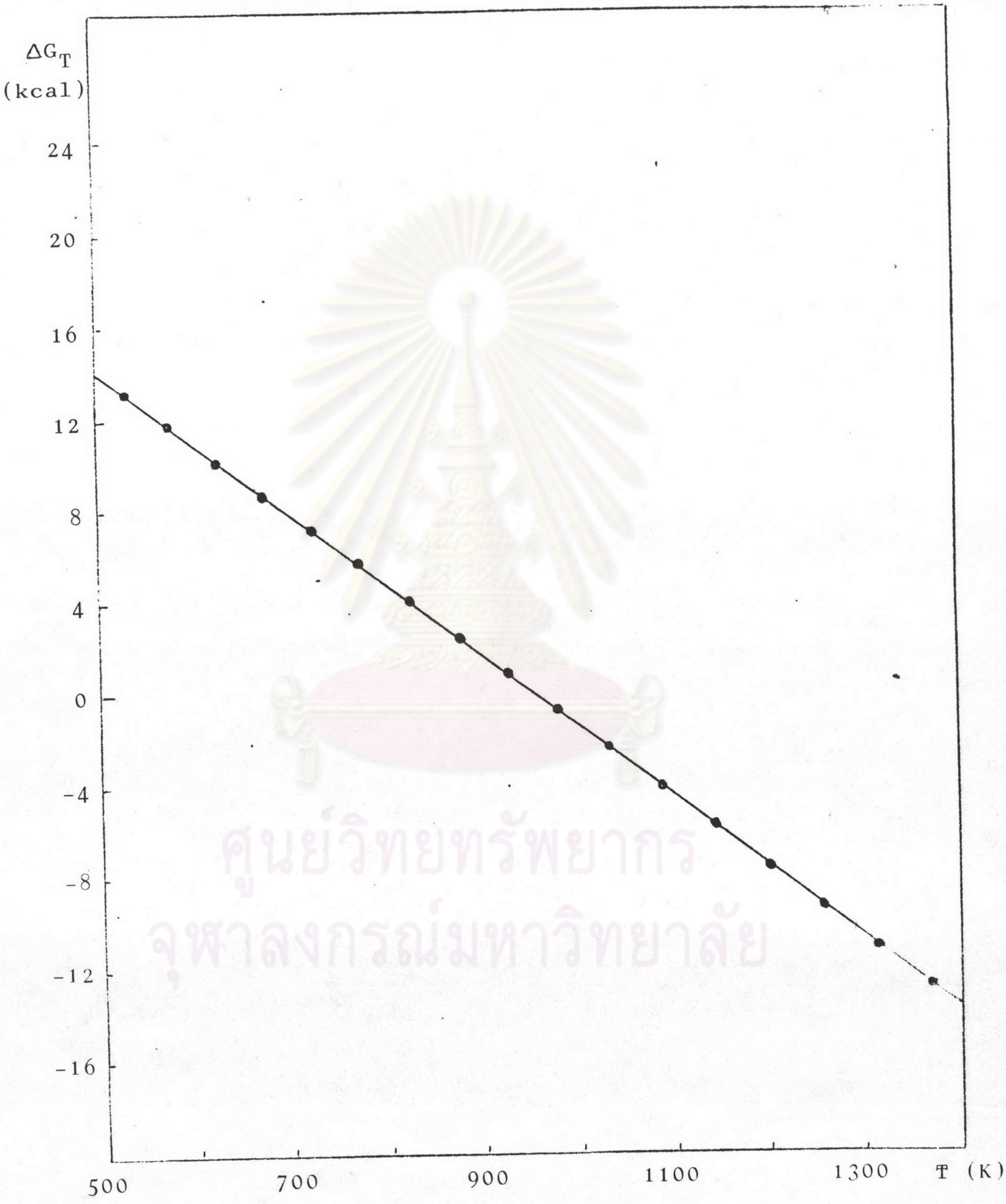

FIG 3.1 THE CORRELATION BETWEEN ΔG_T AND T

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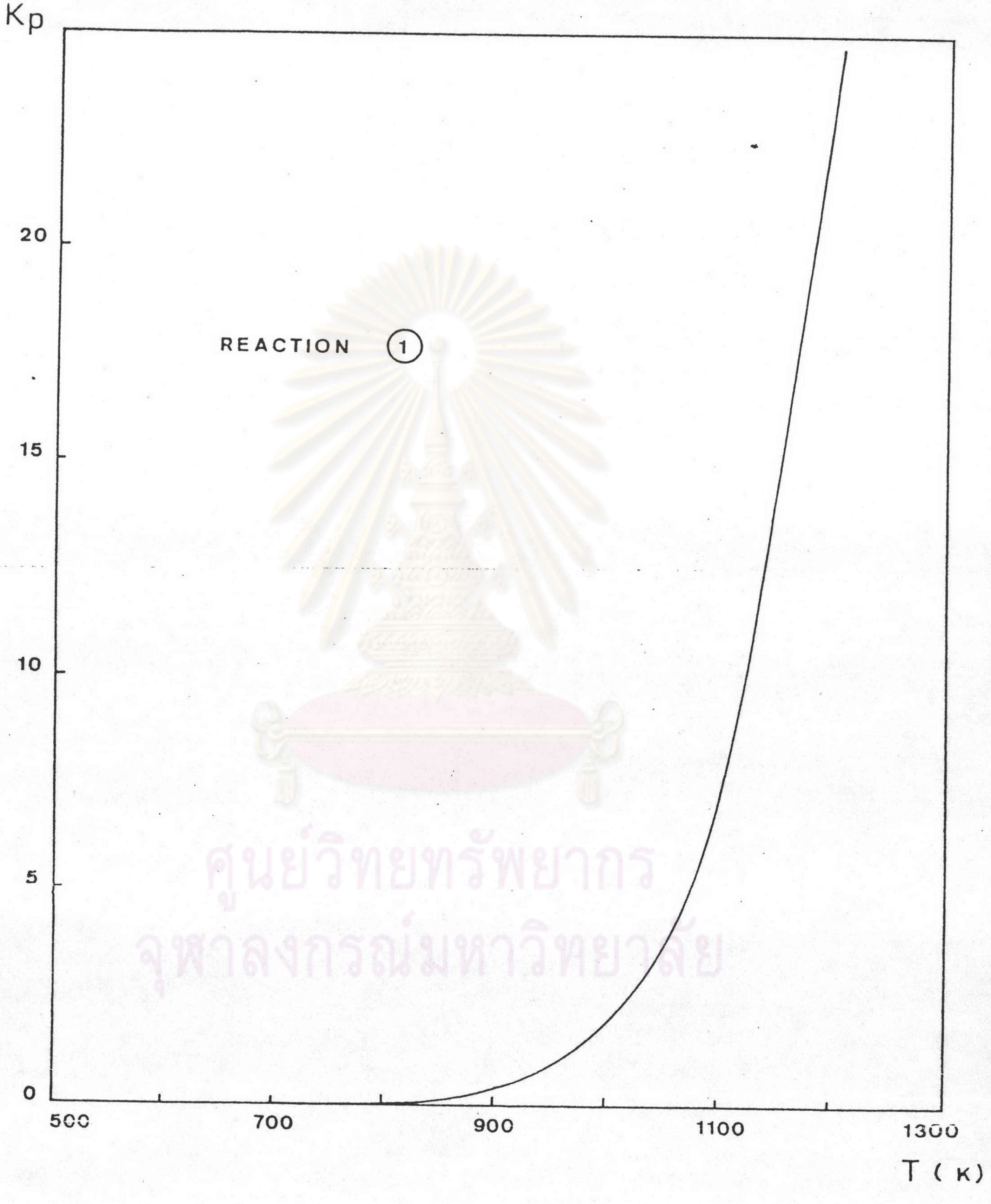

FIG 3.2 THE CORRELATION BETWEEN K_p AND T

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3.2 Determination the rate of equilibrium conversion

In the equilibrium conversion, we can determine the conversion of the reactant from the relation of conversion and the equilibrium constant. The equilibrium constant can be calculated from the thermogynamics data.

For the dehydrogenation of ethylbenzene to styrene

$$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CHCH_2 + H_2$$

The relationship between the conversion and the equilibrium constant is

$$K_p = \frac{X^2P}{1-X^2} \tag{8}$$

where K_p = equilibrium constant

X = conversion of ethylbenzene

P = total pressure

Generally, for the dehydrogenation of the ethylbenzene to styrene, the reaction always occurs in the case that we add some diluent to improve yields and conversion. The diluent added the system can be mainly categorized as

1. The diluent not reacting with ethylbenzene, for example, inert gas, H_2O.
2. The diluent reacting with ethylbenzene, for example, CO_2, SO_2.

a. In the case of the diluent not reacting with ethylbenzene such as steam. The reaction is

$$C_6H_5CH_2CH_3 + H_2O \rightleftharpoons C_6H_5CHCH_3 + H_2O + H_2$$

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The relationship between the conversion and the equilibrium constant is

$$K_p = \frac{X^2 P}{(1-X)(1+X+r')} \qquad (9)$$

where r' = mole ratio of steam to ethylbenzene

b. In the case of the diluent reacting with the ethylbenzene such as CO_2. The reaction can be written as

$$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CHCH_2 + H_2$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

The overall reaction is

$$C_6H_5CH_2CH_3 + CO_2 \rightleftharpoons C_6H_5CHCH_2 + H_2O + CO$$

The relationship between the conversion and the equilibrium constant is

$$K_p = \frac{X^3 P}{(1+X+r'')(1-X)(r''-X)} \qquad (10)$$

where r" = mole ratio of carbon dioxide to ethylbenzene

From the equation (8), (9), (10) and data in table 3.3, the value of equilibrium conversion at various temperature and diluent can determine. The sample of calculation is shown in appendix F

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Table 3.4

Equilibrium conversion at various temperature and diluent

T (K)	K_p	%X			
		P_{EB}=1atm	P_{EB}=0.067atm H_2O/EB=1	P_{EB}=0.018atm H_2O/EB=17.69	P_{EB}=0.067atm CO_2/EB=13.86
500	7.067×10^{-7}	0.084	0,12	0.36	5.15
600	9.33×10^{-5}	0.96	1.36	4.09	24.39
700	3.152×10^{-3}	5.61	7.72	21.61	62.39
800	4.49×10^{-2}	20.73	27.24	59.34	91.62
900	0.3584	51.36	60.64	88.77	98.68
1000	1.8963	80.92	86.28	97.45	99.74
1100	7.4278	93.88	95.82	99.32	99.93
1200	23.1851	97.91	98.97	99.78	99.98

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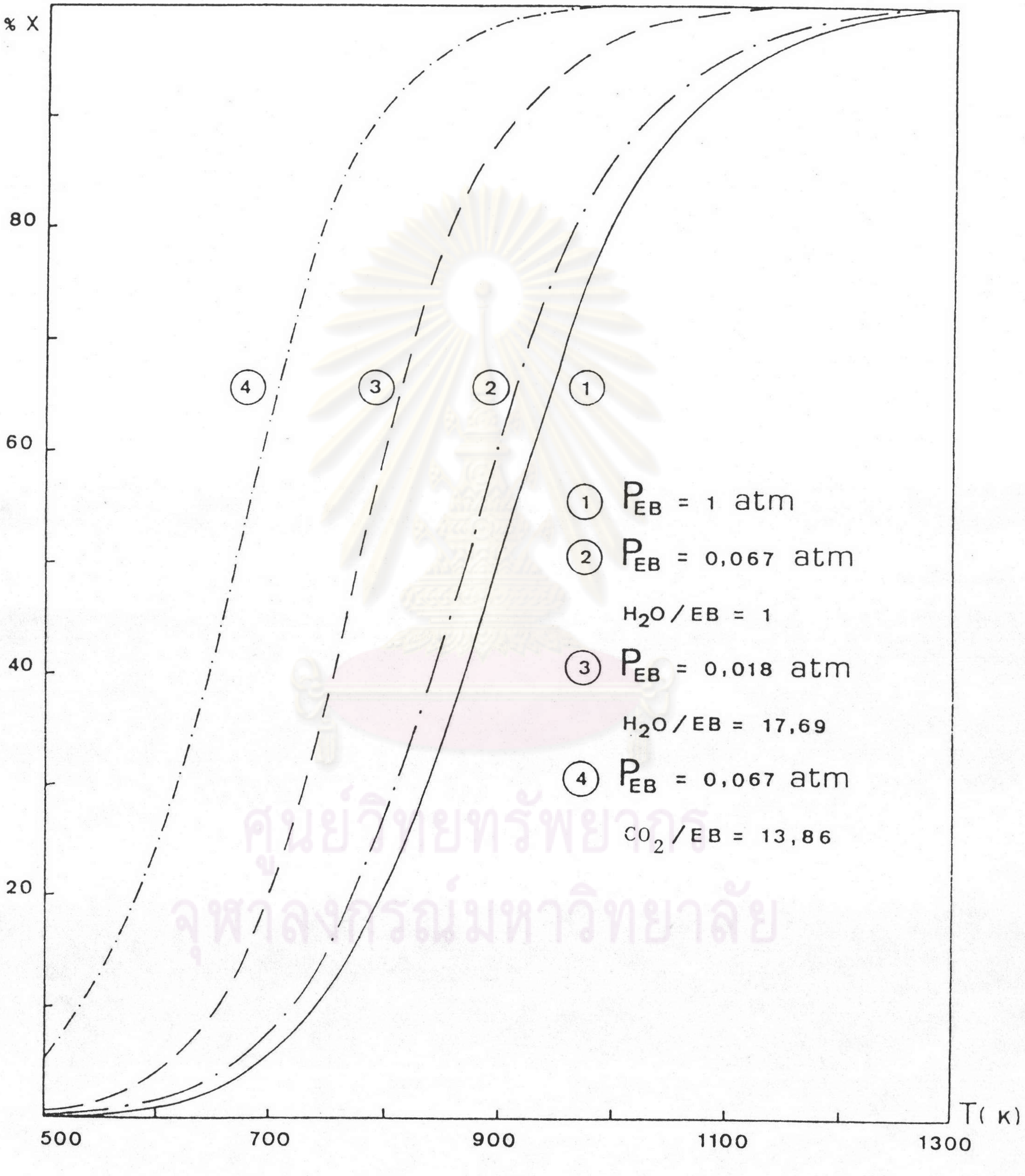

FIG 3.3 EQUILIBRIUM CONVERSION AT VARIOUS TEMPERATURE AND DILUENT

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