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APPENDIX A

THE PHYSICAL PROPERTIES OF ETHYLBENZENE

PROPERTY	T °C	ETHYLBENZENE
Molecular Weight		106.169
Boiling Point		136.19 °C
Critical Density		0.29 gm/cc
Critical Pressure		37 atm
Critical Temperature		346.4 °C
Density	0	0.886 gm/cc
	20	0.867 gm/cc
	40	0.849 gm/cc
	60	0.831 gm/cc
	80	0.814 gm/cc
	100	0.796 gm/cc
Entropy(liquid)	25	60.99 cal/mole °C
(vapor)	25	86.15 cal/mole °C
Free Energy of Formation(liquid)	25	28.614 Kcal/mole
(vapor)	25	31.208 Kcal/mole
Heat of Combustion(liquid)	25	10.2772 Kcal/gm
(vapor)	25	10.3724 Kcal/gm
Heat of Formation(liquid)	25	2.977 Kcal/mole
(vapor)	25	7.120 Kcal/mole
Heat of Fusion		2.190 Kcal/mole

PROPERTY	T (°C)	ETHYLBENZENE
Heat of Vaporization	25	10.097 Kcal/mole
	136.2	8.60 Kcal/mole
Flash Point		15 °C
Freezing Point		-94.975 °C
Ignition Temperature		465 °C
Refractive Index	25	1.4933
Specific Heat(liquid)	-93	0.354 cal/gm °C
	-73	0.360 cal/gm °C
	-53	0.369 cal/gm °C
	-33	0.379 cal/gm °C
	-13	0.391 cal/gm °C
	7	0.405 cal/gm °C
	25	0.420 cal/gm °C
	35	0.430 cal/gm °C
	50	0.450 cal/gm °C
	80	0.495 cal/gm °C
Surface Tension	10	30.2 dynes/cm
	37.8	27.4 dynes/cm
	65.6	24.7 dynes/cm
	93.3	21.9 dynes/cm
	148.9	16.4 dynes/cm
	204.4	10.9 dynes/cm
Vapor Heat Capacity	0	28.19 cal/mole °C
	15.6	29.67 cal/mole °C
	25	30.69 cal/mole °C
	37.8	32.00 cal/mole °C

PROPERTY	T (°C)	ETHYLBENZENE
Vapor Pressure	93.3	37.56 cal/mole °C
	148.9	42.74 cal/mole °C
	260	51.83 cal/mole °C
	537.8	67.58 cal/mole °C
	815.6	77.40 cal/mole °C
	1093.3	83.82 cal/mole °C
	0	1.887 mm Hg
	20	7.067 mm Hg
	40	21.474 mm Hg
	60	55.446 mm Hg
Viscosity	80	125.767 mm Hg
	100	256.922 mm Hg
	120	481.685 mm Hg
	140	840.984 mm Hg
	0	0.8953 cp
	20	0.6783 cp
	40	0.5363 cp
	66	0.4104 cp
Solubility in Water(wt%)	93	0.3254 cp
	149	0.2234 cp
	35	0.02
of Water(wt%)	35	0.063
of Sulphur(wt%)	35	2.61

APPENDIX B

THE PHYSICAL PROPERTIES OF STYRENE

PROPERTY	T (°C)	STYRENE
Molecular Weight		104.153
Boiling Point(1 atm)		145.15 °C
Critical Density		0.297 gm/cc
Critical Pressure		37.8 atm
Critical Temperature		362.1 °C
Critical volume		3.37 cc/gm
Density	0	0.9239 gm/cc
	20	0.9062 gm/cc
	40	0.8885 gm/cc
	60	0.8707 gm/cc
	80	0.8530 gm/cc
	100	0.8353 gm/cc
	120	0.8176 gm/cc
	140	0.7998 gm/cc
Flash Point		31.1 °C
Auto Ignition Temperature		490 °C
Freezing Point		-30.6 °C
Heat of Combustion	25	-1018.83 Kcal/mole
Heat of Formation(gas)	25	35.22 Kcal/mole
(liquid)	25	24.72 Kcal/mole
Heat of Fusion		2360 cal/mole

PROPERTY	T (°C)	STYRENE
Heat of Polymerization	25	16.68 Kcal/mole
Heat of Vaporization	25	100.8 cal/gm
Refractive Index	15	1.5497
	20	1.54862
	25	1.54395
	30	1.54108
	35	1.53821
Solubility in Acetone	25	∞
Carbon Tetrachloride	25	∞
Benzene	25	∞
n-Heptane	25	∞
Ethanol	25	∞
Water(%)	25	0.032
Water in(%)	25	0.070
Specific Heat(liquid)	0	0.4004 cal/gm °C
	20	0.4131 cal/gm °C
	40	0.4269 cal/gm °C
	60	0.4421 cal/gm °C
	80	0.4590 cal/gm °C
	100	0.4774 cal/gm °C
	120	0.4969 cal/gm °C
	140	0.5174 cal/gm °C
(vapor)	25	0.2802 cal/gm °C

PROPERTY	T (°C)	STYRENE	
Surface Tension	0	34.5	dynes/cm
	20	32.3	dynes/cm
	40	30.0	dynes/cm
	60	27.8	dynes/cm
	80	25.6	dynes/cm
	100	23.5	dynes/cm
	120	21.5	dynes/cm
	140	19.4	dynes/cm
Vapor Pressure	0	1.15	mm Hg
	20	4.50	mm Hg
	40	14.30	mm Hg
	60	38.41	mm Hg
	80	90.31	mm Hg
	100	190.63	mm Hg
	120	368.22	mm Hg
	140	660.64	mm Hg
Viscosity	0	1.039	cp
	20	0.762	cp
	40	0.588	cp
	60	0.469	cp
	80	0.385	cp
	100	0.324	cp
	120	0.279	cp
	140	0.243	cp

PROPERTY	T (°C)	STYRENE
Cubic Coefficient of Expansion	20	9.783×10^{-4}
	30	9.879×10^{-4}
	40	9.978×10^{-4}
Q Value		1.0
E Value		-0.8
Volumetric Shrinkage upon Polymerization(%)		17.0



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APPENDIX C



THERMODYNAMIC OF REACTION

Equation use for calculate the thermodynamic properties of the reaction are

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

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

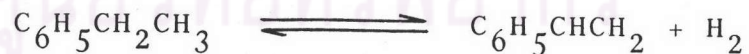
$$\Delta H_T(R) = \Delta H_{298}(R) + \int_{298}^T \Delta C_p(R) dT$$

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

$$\Delta C_p = \Delta C_p(\text{product}) - \Delta C_p(\text{reactant})$$

$$C_p = a + bT + cT^2 + dT^3$$

The thermodynamic properties of ethylbenzene dehydrogenation to styrene are



The value of the constant a, b, c, d for C_p are as followed

Substances	a	$bx10^2$	$cx10^5$	$dx10^9$
Ethylbenzene	-8.398	15.935	-10.003	23.95
Styrene	-5.968	14.354	-9.15	22.03
Hydrogen	6.952	-0.04576	0.09563	-0.2079

$$C_p(R) = -8.398 + 15.935 \times 10^{-2} T - 10.003 \times 10^{-5} T^2 + 23.95 \times 10^{-9} T^3$$

$$C_p(S) = -5.968 + 14.354 \times 10^{-2} T - 9.15 \times 10^{-5} T^2 + 22.03 \times 10^{-9} T^3$$

$$C_p(H) = 6.952 - 0.04576 \times 10^{-2} T + 0.09563 \times 10^{-5} T^2 - 0.2079 \times 10^{-9} T^3$$

$$C_p(R) = C_p(H) + C_p(S) - C_p(E)$$

$$= 9.382 - 1.6267 \times 10^{-2} T + 0.949 \times 10^{-5} T^2 - 2.128 \times 10^{-9} T^3$$

$$\int_{298}^T C_p(R)/T \, dT = \left[9.382 \ln T - 1.6267 \times 10^{-2} T + 0.4743 \times 10^{-5} T^2 - 0.71 \times 10^{-9} T^3 \right]_{298}^T$$

$$= -49.0076 + 9.382 \ln T - 1.6267 \times 10^{-2} T + 0.4743 \times 10^{-5} T^2 - 0.7093 \times 10^{-9} T^3$$

$$\Delta S_{298}(R) = 27.5288$$

$$\Delta S_T(R) = \Delta S_{298}(R) + \int_{298}^T \Delta C_p(R)/T \, dT$$

$$= -21.4788 + 9.382 \ln T - 1.6267 \times 10^{-2} T + 0.4743 \times 10^{-5} T^2 - 0.7093 \times 10^{-9} T^3$$

$$\int_{298}^T C_p(R) \, dT = \left[9.382 T - 0.8134 \times 10^{-2} T^2 + 0.3162 \times 10^{-5} T^3 - 0.532 \times 10^{-9} T^4 \right]_{298}^T$$

$$= -2153.86 - 0.8134 \times 10^{-2} T^2 + 9.382 T + 0.3162 \times 10^{-5} T^3 - 0.832 \times 10^{-9} T^4$$

$$\Delta H_{298}(R) = 28100$$

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

$$= 25946.1415 + 9.382 T - 0.8134 \times 10^{-2} T^2 + 0.3162 \times 10^{-5} T^3 - 0.5319 \times 10^{-9} T^4$$

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

$$= 25946.1415 - 9.382 T \ln T + 30.8608 T + 0.8134 \times 10^{-2} T^2 - 0.158 \times 10^{-5} T^3 + 0.1773 \times 10^{-9} T^4$$

$$\ln K_p = \Delta G_T(R)/RT$$

T (K)	ΔG_T (kcal)	K_p
500	14.0709	7.0649×10^{-7}
600	11.0629	9.3322×10^{-5}
700	8.0114	3.1515×10^{-3}
800	4.9322	4.4924×10^{-2}
900	1.8358	0.3582
1000	-1.2703	1.8952
1100	-4.381	7.4225
1200	-7.4934	23.1663

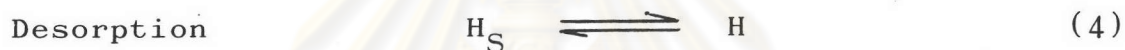
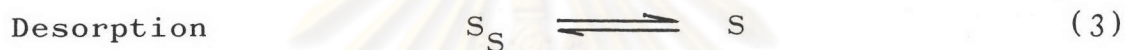
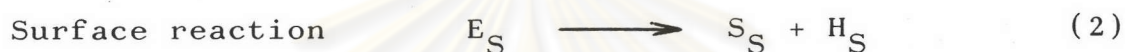
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APPENDIX D

DETERMINATION OF RATE EQUATION



Mechanism 1



The rate equation of the above reactions are

$$r_1 = k_1 P_R \theta_o - k_1^{-1} \theta_E$$

$$r_2 = k_2 \theta_E - k_2^{-1} \theta_S P_H$$

$$r_3 = k_3 P_S \theta_o - k_3^{-1} \theta_S$$

$$r_4 = k_4 P_H \theta_o - k_4^{-1} \theta_H$$

$$r_5 = k_5 P_I \theta_o - k_5^{-1} \theta_I$$

Apply Langmuir-Hinshelwood model by assume

1. Surface reaction is rate controlling step.
2. Adsorption and desorption step are in equilibrium.

So $r_1 = r_3 = r_4 = r_5 = 0$

Obtain $\theta_E = b_1 P_E \theta_o$

$$\theta_S = b_3 P_S \theta_o$$

$$\theta_H = b_4 P_H \theta_o$$

$$\theta_I = b_5 P_I \theta_o$$

$$r_2 = k_2 \theta_E - k_2^{-1} \theta_S P_H$$

$$= k_2 (\theta_E - \theta_S P_H / K_2)$$

$$= k_2 b_1 \theta_o (P_E - P_S P_H / K) \quad (K = K_2 / b_1 b_3)$$

From

$$1 = \theta_S + \theta_E + \theta_H + \theta_I + \theta_o$$

$$1 = b_3 P_S \theta_o + b_1 P_E \theta_o + b_4 P_H \theta_o + b_5 P_I \theta_o + \theta_o$$

$$\theta_o = 1 / (1 + b_1 P_E + b_3 P_S + b_4 P_H + b_5 P_I)$$

$$r_2 = \frac{k_2 b_1 (P_E - P_S P_H / K)}{(1 + b_1 P_E + b_3 P_S + b_4 P_H + b_5 P_I)} \quad (1)$$

where r_i = rate of reaction i
 k_i = forward rate constant of reaction i
 k_i^{-1} = reverse rate constant of reaction i
 K_i = equilibrium constant of reaction i
 P_j = partial pressure of component j
 θ_j = mole fraction of component j in active site
of catalyst

b_1, b_3, b_4, b_5 = adsorption co-efficient of ethylbenzene,
styrene, hydrogen, impurity

subscript E = ethylbenzene

S = styrene

H = hydrogen

I = impurity

o = vacant site

Mechanism 2



The rate equation of the above reaction are

$$r_1 = k_1 P_E \theta_o - k_1^{-1} \theta_E$$

$$r_2 = k_2 \theta_E$$

Apply Langmuir-Hinshelwood model by assume

1. Surface reaction is rate controlling step.
2. Adsorption step is in equilibrium.

So $r_1 = 0$

Obtain $\theta_E = b_1 P_E \theta_o$

$$r_2 = k_2 b_1 P_E \theta_o$$

From $1 = \theta_o + \theta_E$

$$1 = \theta_o + b_1 P_E \theta_o$$

$$\theta_o = 1 / (1 + b_1 P_E)$$

$$r_2 = \frac{k_2 b_1 P_E}{1 + b_1 P_E} \quad (2)$$

or $\frac{1}{r_2} = \frac{1}{k_2} + \frac{1}{k_2 b_1 P_E}$

APPENDIX E

SAMPLE OF CALCULATION

Determine the rate equation

Reactor temperature	360	C
Flow rate CO ₂	1.465x10 ⁻⁵	mole/sec
Partial pressure ethylbenzene	11.15	mm Hg
Weight catalyst	0.26	gm
Area styrene detect	100.45	mm ²
Standard: area styrene 131.48 mm ²	1.728x10 ⁻⁸	mole
Area styrene detect 100.45 mm ²	1.32x10 ⁻⁸	mole
Sampling loop 2 ml, 110 C, 1 atm.		

From $PV = nRT$

where P = pressure (1atm)

V = volume (2cc)

n = number of mole

R = gas constant (82.057)

T = absolute temperature (383 K)

Thus $n = 6.3638 \times 10^{-5}$ mole

Mole of ethylbenzene in sampling loop

$$= \frac{\text{partial pressure}}{\text{total pressure}} \times \text{mole in sampling loop}$$

$$= \frac{11.15}{760} \times 6.3638 \times 10^{-5}$$

$$= 9.336 \times 10^{-7} \text{ mole}$$

$$\begin{aligned} \% \text{ conversion} &= \frac{\text{mole styrene}}{\text{mole ethylbenzene}} \times 100 \\ &= \frac{1.32 \times 10^{-8}}{9.336 \times 10^{-7}} \times 100 \\ &= 1.414 \end{aligned}$$

$$P_E = 11.15$$

$$\frac{1}{P_E} = 0.0897$$

$$P_E + P_{CO_2} = 760$$

mm Hg

$$11.15 + P_{CO_2} = 760$$

$$P_{CO_2} = 748.85$$

mm Hg

$$\begin{aligned} \text{Flow rate ethylbenzene} &= \frac{P_E}{P_{CO_2}} \times \text{flow rate } CO_2 \\ &= \frac{11.15}{748.85} \times 1.465 \times 10^{-5} \\ &= 2.1813 \times 10^{-7} \end{aligned}$$

$$r = \frac{FX}{W}$$

$$= \frac{2.1813 \times 10^{-7} \times 0.01414}{0.26}$$

$$= 1.1863 \times 10^{-8}$$

$$\frac{1}{r} = 84295867$$

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APPENDIX F

SAMPLE OF CALCULATION OF EQUILIBRIUM CONSTANT

From equation (8), (9), (10) and table 3.3

equation (8)
$$K_p = \frac{X^2 P}{1-X^2}$$

where $K_p = 7.067 \times 10^{-7}$ at 500 K
 $P = 1$ atm

$$X = 0.00084$$

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

where $K_p = 7.067 \times 10^{-7}$ at 500 K
 $P = 1$ atm

$$r' = 1$$

$$X = 0.0012$$

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

where $K_p = 7.067 \times 10^{-7}$ at 500 K
 $P = 1$ atm

$$r'' = 13.68$$

$$X = 0.0515$$

AUTOBIOGRAPHY

Mr. Pornlert Prichayudh was born on December 13, 1959 in Bangkok, Thailand. He was graduate in Chemical Engineering from Chulalongkorn University in 1981 and continued his Master's degree study in Chemical Engineering Chulalongkorn University in June 1981.



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