HW#2 Problem 1

Vinyl chloride can be synthesized by reaction of acetylene with hydrochloric acid over a mercuric chloride catalyst at 500K and 5.0 atm total pressure. An undesirable side reaction is the subsequent reaction of vinyl Chloride with HCl. These reactio are illustrated below.

$$HC\equiv CH + HCl \rightleftharpoons H_2C = CHCl$$

$$H_2C = CHCl + HCl \rightleftharpoons H_3C - CHCl_2$$

The equilibrium constants at 500K are 6.6×10^3 and 0.88 for reaction 1 & 2 respectively. Assume ideal behavior.

(a) Find the equilibrium composition at 5.0 atm and 500K for the case when acetylene and HCl are present initially as an equimolar mixture. What is the equilibrium conversion of acetylen ?

	C_2H_2	HCl	C_2H_3Cl	$C_2H_4Cl_2$
I	1	1	0	0
E	$1-\xi_1$	$1-\xi_1-\xi_2$	$\xi_1-\xi_2$	ξ_2

$$\begin{cases} K_1 = 6.6\times10^3 = \dfrac{\left(\frac{\xi_1-\xi_2}{2-\xi_1-\xi_2}\right)}{\left(\frac{1-\xi_1}{2-\xi_1-\xi_2}\right)\cdot\left(\frac{1-\xi_1-\xi_2}{2-\xi_1-\xi_2}\right)}\cdot\left(\frac{5}{1}\right)^{-1} \\ K_2 = 0.88 = \dfrac{\left(\frac{\xi_2}{2-\xi_1-\xi_2}\right)}{\left(\frac{\xi_1-\xi_2}{2-\xi_1-\xi_2}\right)\cdot\left(\frac{1-\xi_1-\xi_2}{2-\xi_1-\xi_2}\right)}\cdot\left(\frac{5}{1}\right)^{-1} \end{cases}$$

Solve the abovementioned equations and get,

$$\begin{cases} \xi_1 = 0.9875 \\ \xi_2 = 0.0102 \end{cases}$$

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Final composition:

$$[C_2H_2] = \frac{1-\xi_1}{2-\xi_1-\xi_2} = 0.0125 \qquad [HCl] = \frac{1-\xi_1-\xi_2}{2-\xi_1-\xi_2} = 0.0023$$

$$[C_2H_3Cl] = \frac{\xi_1-\xi_2}{2-\xi_1-\xi_2} = 0.975 \qquad [C_2H_4Cl_2] = \frac{\xi_2}{2-\xi_1-\xi_2} = 0.0102$$

(b) Redo part (a) with a large excess of inert gas. Assume the inert gas constitutes 90% of the initial gas volume.

	C_2H_2	HCl	C_2H_3Cl	$C_2H_4Cl_2$	N_2
I	1	1	0	0	18
E	$1-\xi_1$	$1-\xi_1-\xi_2$	$\xi_1-\xi_2$	ξ_2	18

$$K_1 = 6.6\times10^3 = \frac{\left(\frac{\xi_1-\xi_2}{20-\xi_1-\xi_2}\right)}{\left(\frac{1-\xi_1}{20-\xi_1-\xi_2}\right)\cdot\left(\frac{1-\xi_1-\xi_2}{20-\xi_1-\xi_2}\right)}\cdot\left(\frac{5}{1}\right)^{-1}$$

$$K_2 = 0.88 = \frac{\left(\frac{\xi_2}{20-\xi_1-\xi_2}\right)}{\left(\frac{\xi_1-\xi_2}{20-\xi_1-\xi_2}\right)\cdot\left(\frac{1-\xi_1-\xi_2}{20-\xi_1-\xi_2}\right)}\cdot\left(\frac{5}{1}\right)^{-1}$$

Solve them, and get $\begin{cases}\xi_1 = 0.94666\\ \xi_2 = 0.00223\end{cases}$

The equilibrium conversion of acetylene is 94.67%

Final Composition:

$$[C_2H_2] = \frac{1-\xi_1}{20-\xi_1-\xi_2} = 0.0028 \qquad [HCl] = \frac{1-\xi_1-\xi_2}{20-\xi_1-\xi_2} = 0.0027$$

$$[C_2H_3Cl] = \frac{\xi_1-\xi_2}{20-\xi_1-\xi_2} = 0.04957 \qquad [C_2H_4Cl_2] = \frac{\xi_2}{20-\xi_1-\xi_2} = 0.00012$$

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Problem # 2 → Probl 7, Ch 1, DD

Integrated Rate Law for a 2nd order Rxn.

$$A + B \longrightarrow C$$

$$r = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A][B]$$

Because [A] = [B] (equimolar)

$$r = K[A]^2 = -\frac{d[A]}{dt}$$

Rearranging:

$$\frac{d[A]}{[A]^2} = -k\,dt$$

Integrate:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

$$kt = \frac{1}{[A]_t} - \frac{1}{[A]_0}$$

$$\boxed{k = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{\Delta t}}$$ //

or

$$\underset{\downarrow}{\frac{1}{[A]_t}} = \underset{\downarrow\ \downarrow}{kt} + \underset{\downarrow}{\frac{1}{[A]_0}}$$

$$y = mx + b$$

T(K)	t(h)	[A] = [B] (mol/L)
323	0	0.097
323	20	0.079

$$k_{323} = \frac{\frac{1}{0.079\frac{mol}{L}} - \frac{1}{0.097\frac{mol}{L}}}{(20-0)h} = 0.117 \frac{L}{M \cdot h}$$

or $0.117 \frac{L}{mol \cdot h}$

or $3.26 \times 10^{-5} \frac{L}{mol \cdot s}$

Better approach

* You can also plot → more precise

$\frac{1}{[A]_t}$ vs t

* The slope of the graph is the value of "k" → rate constant.

* Please look at Excel sheet

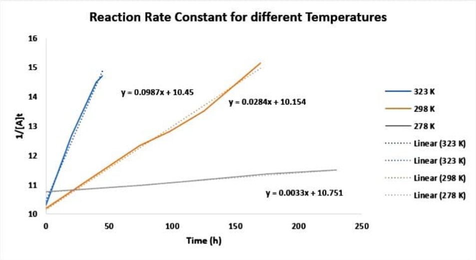
$$\boxed{k_{323} = 0.0987 \frac{L}{mol \cdot h}}$$ //

$$\boxed{k_{298} = 0.0284 \frac{L}{mol \cdot h}}$$ //

$$\boxed{k_{278} = 0.0033 \frac{L}{mol \cdot h}}$$ //

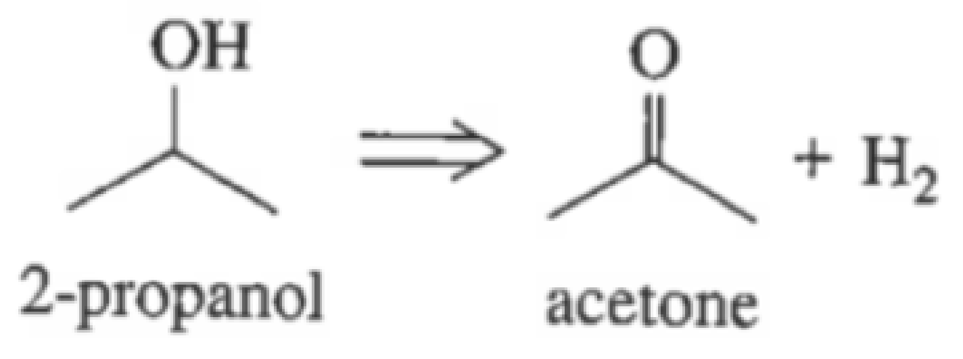
T (K)	t(h)	Δt	[A] = [B] (mol/L)	1/[A]	k (L/mol*h)	k (L/mol*s)
323	0	0	0.097	10.30927835		
323	20	20	0.079	12.65822785	0.117447475	3.26243E-05
323	40	20	0.069	14.49275362	0.091726289	2.54795E-05
323	45	5	0.068	14.70588235	0.042625746	1.18405E-05
298	0	0	0.098	10.20408163		
298	74	74	0.081	12.34567901	0.028940505	8.03903E-06
298	98	24	0.078	12.82051282	0.019784742	5.49576E-06
298	125	27	0.074	13.51351351	0.025666692	7.12964E-06
298	170	45	0.066	15.15151515	0.036400036	1.01111E-05
278	0	0	0.093	10.75268817		
278	75	75	0.091	10.98901099	0.003150971	8.7527E-07
278	110	35	0.09	11.11111111	0.003488575	9.69049E-07
278	176	66	0.088	11.36363636	0.00382614	1.06282E-06
278	230	54	0.087	11.49425287	0.002418824	6.71896E-07

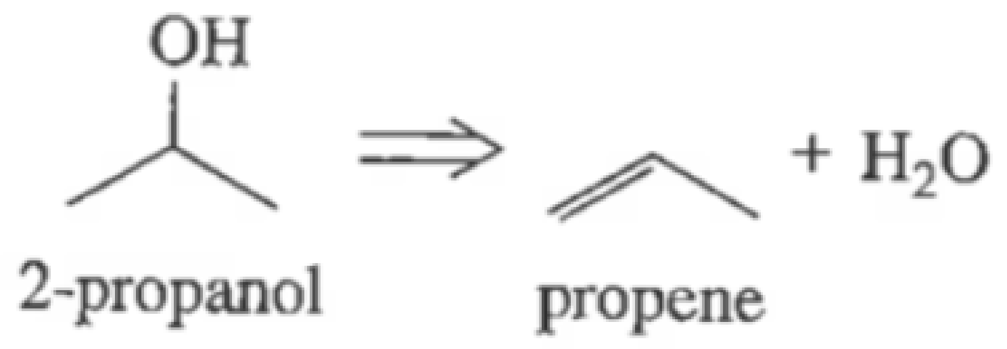
T (K)	k (L/mol*h)
323	0.0987
323	0.0284
323	0.0033


Reaction Rate Constant for different Temperatures
1/[A]t
16
15
14
13
12
11
10
0
50
100
150
200
250
Time (h)
y = 0.0987x + 10.45
y = 0.0284x + 10.154
y = 0.0033x + 10.751
323 K
298 K
278 K
Linear (323 K)
Linear (323 K)
Linear (298 K)
Linear (278 K)

3.

2. The decomposition of gaseous 2-propanol over a mixed oxide catalyst of magnesia and alumina produces both acetone and propene according to the following equations:





From the data presented below, calculate the activation energy for each reaction (A. L. McKenzie, M.S. Thesis, Univ. of Virginia, 1992). Assume the concentration of 2-propanol is constant for each experiment. Selectivity to acetone is defined with respect to the products acetone and propene.

Temperature (K)	573	583	594	603	612
Rate of acetone formation (mol gcat^{-1} s^{-1})	4.1×10^{-7}	7.0×10^{-7}	1.4×10^{-6}	2.2×10^{-6}	3.6×10^{-6}
Selectivity to acetone (%)	92	86	81	81	81

$$\text{Selectivity} = \frac{R_{\text{acetone}}}{R_{\text{acetone}} + R_{\text{propene}}}$$

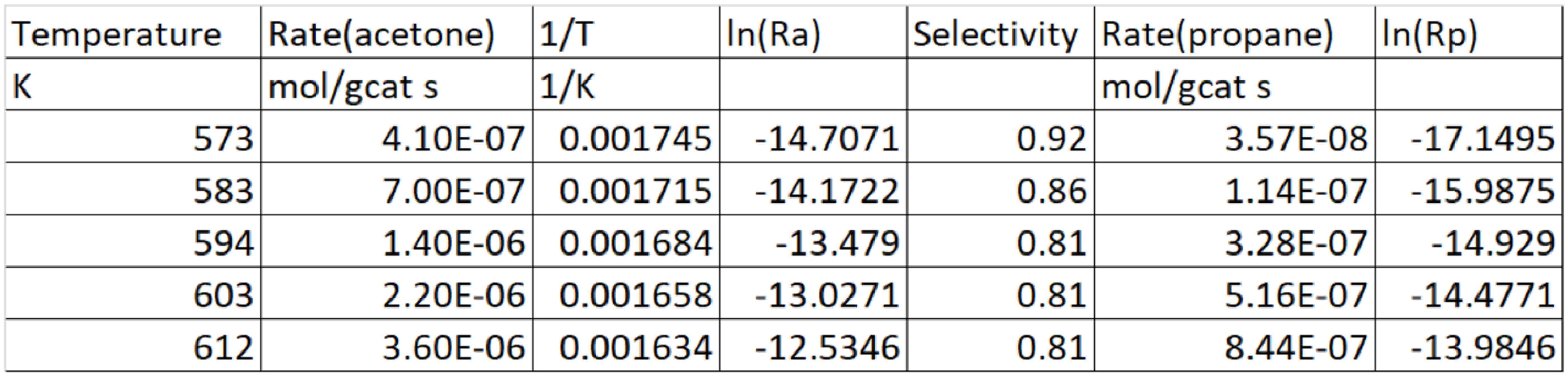
$$R_p = \frac{R_a - S \cdot R_a}{S}$$

$$R = k\, C_{\text{propanol}}$$

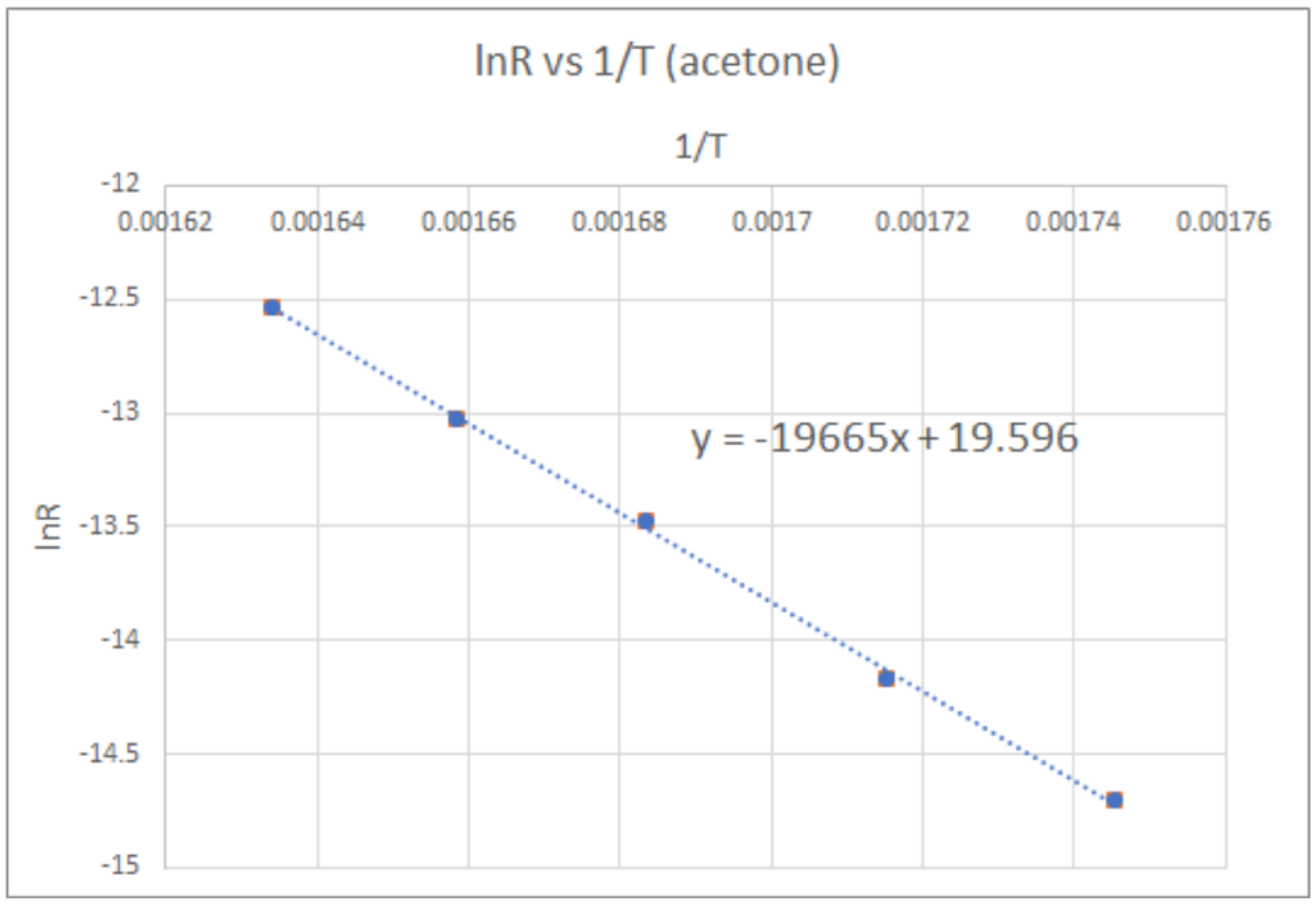
$$R = A \exp\left(\frac{-E_a}{RT}\right) \cdot C_p$$

$$\ln R = \underbrace{\ln A C_p}_{\text{constant}} - \underbrace{\frac{E_a}{R}}_{\text{constant}} \cdot \frac{1}{T}$$

plot $\ln R$ vs. $\frac{1}{T}$ ⇒ find slope



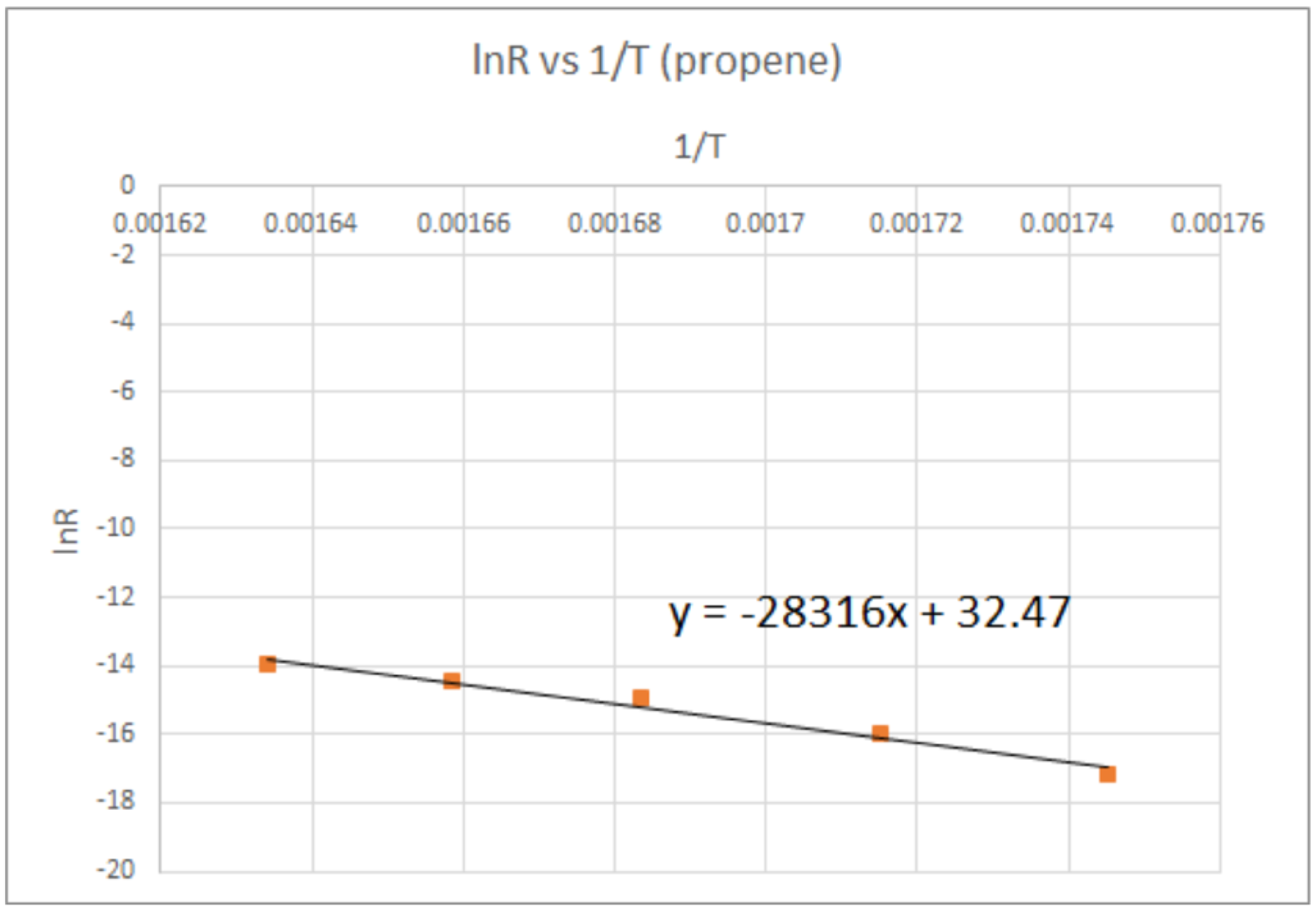
Temperature	Rate(acetone)	1/T	ln(Ra)	Selectivity	Rate(propane)	ln(Rp)
K	mol/gcat s	1/K			mol/gcat s	
573	4.10E-07	0.001745	-14.7071	0.92	3.57E-08	-17.1495
583	7.00E-07	0.001715	-14.1722	0.86	1.14E-07	-15.9875
594	1.40E-06	0.001684	-13.479	0.81	3.28E-07	-14.929
603	2.20E-06	0.001658	-13.0271	0.81	5.16E-07	-14.4771
612	3.60E-06	0.001634	-12.5346	0.81	8.44E-07	-13.9846



$$-19665 = -\frac{Ea}{R}$$

$$Ea = 19965 \times 8.314$$

$$= 1.66 \times 10^5 \ J/mol$$



$$Ea = 28316 \times 8.314$$

$$= 2.35 \times 10^5 \ J/mol$$