

# Montogue

## QUIZ CE105

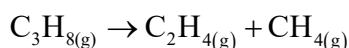
### Chemical Equilibrium Thermodynamics

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#### ► PROBLEMS

##### ► Problem 1 (Smith et al., 2004, w/ permission)

For the cracking reaction,

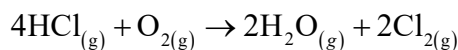


the equilibrium conversion is negligible at 300 K, but becomes appreciable at temperatures above 500 K. For a pressure of 1 bar, determine the fractional conversion of propane at 625 K.

- A)  $\varepsilon = 0.263$
- B)  $\varepsilon = 0.501$
- C)  $\varepsilon = 0.780$
- D)  $\varepsilon = 0.925$

##### ► Problem 2 (Smith et al., 2004, w/ permission)

The following reaction reaches equilibrium at 500°C and 1 bar:

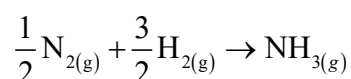


If the system initially contains 5 mol of HCl for each mole of oxygen, what is the composition of the system at equilibrium? Assume ideal gases.

Component	Equilibrium molar fraction
HCl <sub>(g)</sub>	
O <sub>2(g)</sub>	
H <sub>2</sub> O <sub>(g)</sub>	
Cl <sub>2(g)</sub>	

##### ► Problem 3 (Smith et al., 2004, w/ permission)

For the ammonia synthesis reaction

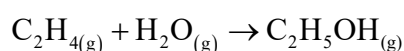


with 0.5 mol N<sub>2</sub> and 1.5 mol H<sub>2</sub> as the initial amounts of reactants and with the assumption that the equilibrium mixture is an ideal gas, show that

$$\varepsilon_e = 1 - \left( 1 + 2.99K \frac{P}{P^0} \right)^{-1/2}$$

##### ► Problem 4 (Smith et al., 2004, w/ permission)

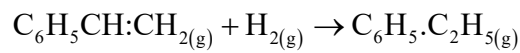
Calculate the equilibrium constant for the vapor-phase hydration of ethylene at 200°C. The reaction in question is of course



- A)  $K = 3.92 \times 10^{-3}$
- B)  $K = 0.0308$
- C)  $K = 0.913$
- D)  $K = 2.72$

► **Problem 5** (Smith et al., 2004, w/ permission)

The following reaction reaches equilibrium at 650°C and atmospheric pressure.

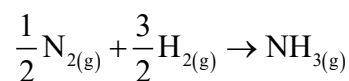


If the system initially contains 1.5 mol H<sub>2</sub> for each mole of styrene, what is the composition of the system at equilibrium? Assume ideal gases.

Component	Equilibrium molar fraction
C <sub>6</sub> H <sub>5</sub> CH:CH <sub>2(g)</sub>	
H <sub>2(g)</sub>	
C <sub>6</sub> H <sub>5</sub> ·C <sub>2</sub> H <sub>5(g)</sub>	

→ **Problem 6.1** (Smith et al., 2004, w/ permission)

For the ammonia reaction,



the equilibrium conversion to ammonia is large at 300 K, but decreases rapidly with increasing *T*. However, reaction rates become appreciable only at higher temperatures. For a feed mixture of hydrogen in the stoichiometric proportions, what is the equilibrium mole fraction of each component at 1 bar and 300 K?

Component	Equilibrium molar fraction
N <sub>2(g)</sub>	
H <sub>2(g)</sub>	
NH <sub>3(g)</sub>	

→ **Problem 6.2**

At what temperature does the equilibrium mole fraction of ammonia equal 0.50 for a pressure of 1 bar?

- A) *T* = 209 K
- B) *T* = 305 K
- C) *T* = 402 K
- D) *T* = 504 K

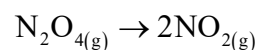
→ **Problem 6.3**

At what temperature does the equilibrium mole fraction of ammonia equal 0.50 for a pressure of 100 bar, assuming the equilibrium mixture is an ideal gas?

- A) *T* = 603 K
- B) *T* = 709 K
- C) *T* = 801 K
- D) *T* = 908 K

► **Problem 7** (Smith et al., 2004, w/ permission)

Species N<sub>2</sub>O<sub>4</sub> and NO<sub>2</sub> as gases come to equilibrium by the equation

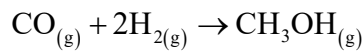


For *T* = 350 K and *P* = 5 bar, calculate the mole fractions of each species in the equilibrium mixture. Assume ideal gases.

Component	Equilibrium molar fraction
N <sub>2</sub> O <sub>4(g)</sub>	
NO <sub>2(g)</sub>	

► **Problem 8** (Smith et al., 2004, w/ permission)

For the methanol synthesis reaction,

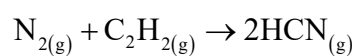


the equilibrium conversion to methanol is large at 300 K, but decreases rapidly with increasing  $T$ . However, reaction rates become appreciable at higher temperatures. For a feed mixture of carbon monoxide and hydrogen in the stoichiometric proportions, what are the equilibrium mole fractions of each component at 1 bar and 300 K?

Component	Equilibrium molar fraction
$\text{CO}_{(g)}$	
$\text{H}_{2(g)}$	
$\text{CH}_3\text{OH}_{(g)}$	

► **Problem 9** (Smith et al., 2004, w/ permission)

The following reaction reaches equilibrium at 650°C and atmospheric pressure:

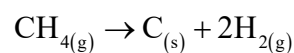


If the system initially is an equimolar mixture of nitrogen and acetylene, what is the composition of the system at equilibrium? Assume ideal gases.

Component	Equilibrium molar fraction
$\text{N}_{2(g)}$	
$\text{C}_2\text{H}_{2(g)}$	
$\text{HCN}_{(g)}$	

► **Problem 10** (Smith et al., 2004, w/ permission)

Carbon black is produced by the decomposition of methane:

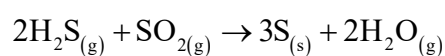


For equilibrium at 650°C and 1 bar, what is the gas-phase composition if pure methane enters the reactor?

Component	Equilibrium molar fraction
$\text{CH}_{4(g)}$	
$\text{H}_{2(g)}$	

► **Problem 11** (Smith et al., 2004, w/ permission)

Oil refineries frequently have both  $\text{H}_2\text{S}$  and  $\text{SO}_2$  to dispose of. The following reaction suggests a means of getting rid of both at once:



For reactants in the stoichiometric proportion, estimate the gas composition if the reaction comes to equilibrium at 450°C and 8 bar.

Component	Equilibrium molar fraction
$\text{H}_2\text{S}_{(g)}$	
$\text{SO}_{2(g)}$	
$\text{H}_2\text{O}_{(g)}$	

## ▶ ADDITIONAL INFORMATION

**Table 1** Standard enthalpies and Gibbs energies of formation at 298.15 K

Compound	Formula	$\Delta H_f^\circ$ (J/mol)	$\Delta G_f^\circ$ (J/mol)
Acetylene	C <sub>2</sub> H <sub>2</sub>	227,480	209,970
Ammonia	NH <sub>3</sub>	-46,110	-16,400
Carbon monoxide	CO	-110,525	-137,169
Dinitrogen tetroxide	N <sub>2</sub> O <sub>4</sub>	9160	9160
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	-235,100	-168,490
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	29,920	130,890
Ethylene	C <sub>2</sub> H <sub>4</sub>	52,510	68,460
Hydrogen chloride	HCl	-92,307	-95,299
Hydrogen cyanide	HCN	135,100	124,700
Hydrogen sulfide	H <sub>2</sub> S	-20,630	-33,560
Methane	CH <sub>4</sub>	-74,520	-50,460
Methanol	CH <sub>3</sub> OH	-200,660	-161,960
Nitrogen dioxide	NO <sub>2</sub>	33,180	51,310
Propane	C <sub>3</sub> H <sub>8</sub>	-104,680	-24,290
Styrene	C <sub>8</sub> H <sub>8</sub>	147,360	213,900
Sulfur dioxide	SO <sub>2</sub>	-296,830	-300,194
Water	H <sub>2</sub> O	-241,818	-228,572

**Table 2** Heat capacity coefficients

Coefficients for use in the equation  $\frac{C_p}{R} = A + BT + CT^2 + DT^{-2}$

With the exception of sulfur and carbon, whose data refer to the solid state, all data are for ideal gases.

Chemical Species	Formula	A	B × 10 <sup>3</sup>	C × 10 <sup>6</sup>	D × 10 <sup>-5</sup>
Acetylene	C <sub>2</sub> H <sub>2</sub>	6.132	1.952	—	-1.299
Ammonia	NH <sub>3</sub>	3.578	3.020	—	-0.186
Carbon (graphite)	C	1.771	0.771	—	-0.867
Carbon monoxide	CO	3.376	0.557	—	-0.031
Chlorine	Cl <sub>2</sub>	4.442	0.089	—	-0.344
Dinitrogen tetroxide	N <sub>2</sub> O <sub>4</sub>	11.66	2.257	—	-2.787
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	3.518	20.001	-6.002	—
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	1.124	55.380	-18.476	—
Ethylene	C <sub>2</sub> H <sub>4</sub>	1.424	14.394	-4.392	—
Hydrogen	H <sub>2</sub>	3.249	0.422	—	0.083
Hydrogen chloride	HCl	3.156	0.623	—	0.151
Hydrogen cyanide	HCN	4.736	1.359	—	-0.725
Hydrogen sulfide	H <sub>2</sub> S	3.931	1.490	—	-0.232
Methane	CH <sub>4</sub>	1.702	9.081	-2.164	—
Methanol	CH <sub>3</sub> OH	2.211	12.216	-3.450	—
Nitrogen	N <sub>2</sub>	3.280	0.593	—	0.040
Nitrogen dioxide	NO <sub>2</sub>	4.982	1.195	—	-0.792
Oxygen	O <sub>2</sub>	3.639	0.506	—	-0.227
Propane	C <sub>3</sub> H <sub>8</sub>	1.213	28.785	-8.824	—
Styrene	C <sub>8</sub> H <sub>8</sub>	2.05	50.192	-16.662	—
Sulfur (rhombic)	S <sub>8</sub>	4.114	-1.728	—	-0.783
Sulfur dioxide	SO <sub>2</sub>	5.699	0.801	—	-1.015
Water	H <sub>2</sub> O	3.470	1.450	—	0.121

## ► SOLUTIONS

### P.1 → Solution

Refer to the following table.

	$C_3H_8(g)$	$\rightarrow$	$C_2H_4(g)$	$CH_4(g)$
$n_0$ (mol)	1		0	0
$n$ (mol)	$1 - \varepsilon$		$\varepsilon$	$\varepsilon$

The fractional conversion of propane is

$$\text{Fractional conversion of } C_3H_8 = \frac{n_0 - n}{n_0} = \frac{1 - (1 - \varepsilon)}{1} = \varepsilon$$

The mole fractions of each component are written as

$$y_{C_3H_8} = \frac{n_{C_3H_8}}{n_T} = \frac{1 - \varepsilon}{1 + \varepsilon}$$

$$y_{C_2H_4} = \frac{n_{C_2H_4}}{n_T} = \frac{\varepsilon}{1 + \varepsilon}$$

$$y_{CH_4} = \frac{n_{CH_4}}{n_T} = \frac{\varepsilon}{1 + \varepsilon}$$

The equilibrium constant is then

$$K = \frac{y_{C_2H_4} y_{CH_4}}{y_{C_3H_8}} = \frac{\left(\frac{\varepsilon}{1 + \varepsilon}\right) \times \left(\frac{\varepsilon}{1 + \varepsilon}\right)}{\left(\frac{1 - \varepsilon}{1 + \varepsilon}\right)}$$

$$\therefore K = \frac{\varepsilon^2}{(1 + \varepsilon)^2} \times \frac{(1 + \varepsilon)}{(1 - \varepsilon)}$$

$$\therefore K = \frac{\varepsilon^2}{1 - \varepsilon^2} \quad (\text{I})$$

Heats of formation at 298 K, taken from Table 1, are listed below.

Compound	$\Delta H_f^\circ$ (J/mol)
$C_3H_8$	-104,680
$CH_4$	-74,520
$C_2H_4$	52,510

The reaction change in enthalpy is found as

$$\Delta H_{298}^\circ = \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants})$$

$$\therefore \Delta H_{298}^\circ = \Delta H_f^\circ (C_2H_4) + \Delta H_f^\circ (CH_4) - \Delta H_f^\circ (C_3H_8)$$

$$\therefore \Delta H_{298}^\circ = 52,510 - 74,520 - (-104,680) = 82,700 \text{ J/mol}$$

Gibbs free energies of formation, also taken from Table 1, are listed below.

Compound	$\Delta G_f^\circ$ (J/mol)
$C_3H_8$	-24,290
$CH_4$	-50,460
$C_2H_4$	68,460

Taking values from Table 1, the variation in free energy for the reaction is

$$\Delta G_{298}^\circ = \Delta G_f^\circ (\text{products}) - \Delta G_f^\circ (\text{reactants})$$

$$\therefore \Delta G_{298}^\circ = \Delta G_f^\circ (C_2H_4) + \Delta G_f^\circ (CH_4) - \Delta G_f^\circ (C_3H_8)$$

$$\therefore \Delta G_{298}^\circ = 68,460 - 50,460 - (-24,290) = 42,300 \text{ J/mol}$$

Coefficients for heat capacities in the ideal-gas state, taken from Table 2, are listed below.

Compound	A	B × 10 <sup>3</sup>	C × 10 <sup>6</sup>	D × 10 <sup>-5</sup>
C <sub>3</sub> H <sub>8</sub>	1.213	28.785	-8.824	0
C <sub>2</sub> H <sub>4</sub>	1.424	14.394	-4.392	0
CH <sub>4</sub>	1.702	9.081	-2.164	0

Parameters  $\Delta A$ ,  $\Delta B$ , and  $\Delta C$  are determined next,

$$\Delta A = A_{CH_4} + A_{C_2H_4} - A_{C_3H_8} = 1.702 + 1.424 - 1.213$$

$$\therefore \Delta A = 1.913$$

$$\Delta B = B_{CH_4} + B_{C_2H_4} - B_{C_3H_8} = (9.081 + 14.394 - 28.785) \times 10^{-3}$$

$$\therefore \Delta B = -5.31 \times 10^{-3}$$

$$\Delta C = C_{CH_4} + C_{C_2H_4} - C_{C_3H_8} = [-2.164 - 4.392 - (-8.824)] \times 10^{-6}$$

$$\therefore \Delta C = 2.268 \times 10^{-6}$$

$$\Delta D = 0$$

Equipped with these quantities, we can evaluate the enthalpy integral

$$\Delta H_{298 \rightarrow 625 \text{ K}} = \int_{298}^{625} C_{P,298}^{\text{ig}} dT$$

$$\therefore \Delta H_{298 \rightarrow 625 \text{ K}} = R \int_{298}^{625} (\Delta A + \Delta B T + \Delta C T^2 + \cancel{\Delta D T^3}) dT$$

$$\therefore \Delta H_{298 \rightarrow 625 \text{ K}} = R \int_{298}^{625} (1.913 - 5.31 \times 10^{-3} T + 2.268 \times 10^{-6} T^2) dT$$

$$\Delta H_{298 \rightarrow 625 \text{ K}} = 8.314 \times (-11.2) = -93.1 \text{ J/mol}$$

In turn, the entropy integral is evaluated as

$$\Delta S_{298 \rightarrow 625} = \int_{298}^{625} \left( \frac{C_{P,298}^{\text{ig}}}{T} \right) dT$$

$$\therefore \Delta S_{298 \rightarrow 625} = R \int_{298}^{625} \left( \Delta A + \Delta B T + \Delta C T^2 + \cancel{\Delta D T^3} \right) \frac{dT}{T}$$

$$\therefore \Delta S_{298 \rightarrow 625} = R \int_{298}^{625} \left( \frac{1.913}{T} - 5.31 \times 10^{-3} + 2.268 \times 10^{-6} T \right) dT$$

$$\Delta S_{298 \rightarrow 625} = 8.314 \times 0.0228 = 0.190 \text{ J/mol} \cdot \text{K}$$

We now have enough information to compute the Gibbs free energy at 625 K, namely

$$\Delta G = \Delta H - T \Delta S$$

$$\therefore \Delta G = \Delta H_{298} + \Delta H_{298 \rightarrow 625} - T (\Delta S_{298} + \Delta S_{298 \rightarrow 625})$$

$$\therefore \Delta G = \Delta H_{298} - T \Delta S_{298} + \Delta H_{298 \rightarrow 625} - T \Delta S_{298 \rightarrow 625}$$

$$\therefore \Delta G = \Delta H_{298} - T \left( \frac{\Delta H_{298} - \Delta G_{298}}{T_0} \right) + \Delta H_{298 \rightarrow 625} - T \Delta S_{298 \rightarrow 625}$$

$$\therefore \Delta G = 82,670 - 625 \left( \frac{82,700 - 42,300}{298} \right) - 93.1 - 625 \times 0.190 = -2270 \text{ J/mol}$$

The equilibrium constant  $K$  is determined next,

$$\Delta G = -RT \ln K \rightarrow K = \exp(-\Delta G/RT)$$

$$\therefore K = \exp[-(-2270)/(8.314 \times 625)] = 1.55$$

We can now substitute  $K$  in equation (I) and solve for  $\epsilon$ ,

$$K = \frac{\varepsilon^2}{1 - \varepsilon^2} \rightarrow 1.55 = \frac{\varepsilon^2}{1 - \varepsilon^2}$$

$$\therefore 1.55 - 1.55\varepsilon^2 = \varepsilon^2$$

$$\therefore \varepsilon = \sqrt{\frac{1.55}{2.55}} = \boxed{0.780}$$

The fractional conversion of propane is 0.78.

♦ The correct answer is **C**.

## P.2 → Solution

To determine the mole fraction of each species, consider the following table.

Species	Initial moles ( $n_{i,0}$ )	Stoichiometric c-fft ( $\nu_i$ )	$n_{i,0} + \nu_i\varepsilon$
HCl	5	-4	$5 - 4\varepsilon$
O <sub>2</sub>	1	-1	$1 - \varepsilon$
H <sub>2</sub> O	0	2	$2\varepsilon$
Cl <sub>2</sub>	0	2	$2\varepsilon$

The total number of moles initially present in the system is  $\Sigma n_{i,0} = 6$ , and the reaction stoichiometric number  $\Sigma \nu = -1$ . The mole fractions are of course expressed as

$$y_i = \frac{n_{i,0} + \nu_i\varepsilon}{n_o + \nu\varepsilon}$$

Applying this relation to each component of the reaction, we get

$$y_{\text{HCl}} = \frac{5 - 4\varepsilon}{6 - \varepsilon}$$

$$y_{\text{O}_2} = \frac{1 - \varepsilon}{6 - \varepsilon}$$

$$y_{\text{H}_2\text{O}} = \frac{2\varepsilon}{6 - \varepsilon}$$

$$y_{\text{Cl}_2} = \frac{2\varepsilon}{6 - \varepsilon}$$

To determine the composition of the system at equilibrium, we need the equilibrium constant  $K$ . This in turn requires the reaction change in Gibbs free energy  $\Delta G$  at the reaction temperature of 773 K, which is given by

$$\frac{\Delta G_{773}}{RT_{773}} = \left( \frac{\Delta G_{298}^\circ - \Delta H_{298}^\circ}{RT_0} \right) + \frac{\Delta H_{298}^\circ}{RT_{773}} + \frac{1}{T_{773}} \int_{298}^{773} \frac{\Delta C_p^\circ}{R} dT - \int_{298}^{773} \frac{\Delta C_p^\circ}{R} \frac{dT}{T} \quad (\text{I})$$

The heats of formation at 298 K, taken from Table 1, are listed below.

Compound	$\Delta H_f^\circ$ (J/mol)
HCl <sub>(g)</sub>	-93,207
O <sub>2(g)</sub>	0
H <sub>2</sub> O <sub>(g)</sub>	-241,818
Cl <sub>2(g)</sub>	0

The reaction  $\Delta H^\circ$  is, accordingly,

$$\Delta H_{298}^\circ = [m\Sigma\Delta H_f^\circ(\text{products})] - [n\Sigma\Delta H_f^\circ(\text{reactants})]$$

$$\therefore \Delta H_{298}^\circ = 2 \times (-241,818) + 2 \times 0 - 4 \times (-92,307) - 1 \times 0$$

$$\therefore \Delta H_{298}^\circ = -114,000 \text{ J/mol}$$

The standard free energies of formation at 298 K, also taken from Table 1, are listed below.

Compound	$\Delta G_f^\circ$ (J/mol)
HCl <sub>(g)</sub>	-95,299
O <sub>2(g)</sub>	0
H <sub>2</sub> O <sub>(g)</sub>	-228,572

Cl <sub>2(g)</sub>	0
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The reaction  $\Delta G_{298}^{\circ}$  follows as

$$\begin{aligned}\Delta G_{298}^{\circ} &= [m \Sigma \Delta G_f^{\circ}(\text{products})] - [n \Sigma \Delta G_f^{\circ}(\text{reactants})] \\ \therefore \Delta G_{298}^{\circ} &= 2\Delta G_{f, \text{H}_2\text{O}}^{\circ} + 2\Delta G_{f, \text{Cl}_2}^{\circ} - 4\Delta G_{f, \text{HCl}}^{\circ} - 1\Delta G_{f, \text{O}_2}^{\circ} \\ \therefore \Delta G_{298}^{\circ} &= 2 \times (-228,572) + 2 \times 0 - 4 \times (-95,299) - 1 \times 0 \\ \therefore \Delta G_{298}^{\circ} &= -75,900 \text{ J/mol}\end{aligned}$$

The heat capacity coefficients for the four compounds in question, taken from Table 2, are listed below.

Compound	A	B × 10 <sup>3</sup>	C × 10 <sup>6</sup>	D × 10 <sup>-5</sup>
HCl <sub>(g)</sub>	3.156	0.623	0	0.151
O <sub>2(g)</sub>	3.639	0.506	0	-0.227
H <sub>2</sub> O <sub>(g)</sub>	3.470	1.45	0	0.121
Cl <sub>2(g)</sub>	4.442	0.089	0	-0.344

Then, we compute the coefficient variations  $\Delta A$ ,  $\Delta B$ , and  $\Delta D$ , namely,

$$\begin{aligned}\Delta A &= \Sigma (v_i A_i) = [(2 \times 3.47) + (2 \times 4.442)] - [(4 \times 3.156) + (1 \times 3.639)] \\ \therefore \Delta A &= -0.439\end{aligned}$$

$$\begin{aligned}\Delta B &= \Sigma (v_i B_i) = \{[2 \times (1.45) + 2 \times (0.089)] - [4 \times (0.623) + 1 \times (0.506)]\} \times 10^{-3} \\ \therefore \Delta B &= 8 \times 10^{-5}\end{aligned}$$

$$\Delta C = \Sigma (v_i C_i) = 0$$

$$\begin{aligned}\Delta D &= \Sigma (v_i D_i) = \{[2 \times (0.121) + 2 \times (-0.344)] - [4 \times (0.151) + 1 \times (-0.227)]\} \times 10^5 \\ \therefore \Delta D &= -82,300\end{aligned}$$

Instead of evaluating the integrals directly as was done in Problem 1, we will employ the formulas devised in the textbook by Smith et al. These expressions require the temperature ratio  $\tau = 773/298 = 2.59$ . The first formula is

$$\begin{aligned}\int_{298}^{773} \frac{\Delta C_p^{\circ}}{R} dT &= \left[ \Delta A T_0 (\tau - 1) + \frac{\Delta B T_0^2 (\tau^2 - 1)}{2} + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right) \right] \\ \therefore \int_{298}^{773} \frac{\Delta C_p^{\circ}}{R} dT &= \left[ -0.439 \times 298 \times (2.59 - 1) + \frac{(8 \times 10^{-5}) \times 298^2 \times (2.59^2 - 1)}{2} + 0 + \frac{(-82,300)}{298} \left( \frac{2.59 - 1}{2.59} \right) \right] \\ \therefore \int_{298}^{773} \frac{\Delta C_p^{\circ}}{R} dT &= -357\end{aligned}$$

The second formula is

$$\begin{aligned}\int_{298}^{773} \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T} &= \Delta A \ln \tau + \left[ \Delta B T_0 + \left( \Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2} \right) \left( \frac{\tau + 1}{2} \right) \right] (\tau - 1) \\ \therefore \int_{298}^{773} \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T} &= -0.439 \times \ln(2.59) + \left\{ (8 \times 10^{-5}) \times 298 + \left[ 0 + \frac{(-82,300)}{2.59^2 \times 298^2} \right] \times \left( \frac{2.59 + 1}{2} \right) \right\} (2.59 - 1) \\ \therefore \int_{298}^{773} \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T} &= -0.774\end{aligned}$$

Returning to equation (I) and recalling that  $\ln K = -\Delta G/RT$ , we have

$$\begin{aligned}\Delta G &= -RT \ln K \rightarrow -\ln K = \frac{\Delta G}{RT} \\ \therefore -\ln K &= \left( \frac{\Delta G_{298}^{\circ} - \Delta H_{298}^{\circ}}{RT_0} \right) + \frac{\Delta H_{298}^{\circ}}{RT_{773}} + \frac{1}{T_{773}} \int_{298}^{773} \frac{\Delta C_p^{\circ}}{R} dT - \int_{298}^{773} \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T}\end{aligned}$$



$$\therefore -\ln K = \left[ \frac{-75,900 - (-114,000)}{8.314 \times 298} \right] + \frac{(-114,000)}{8.314 \times 773} + \frac{1}{773} \times (-357) - (-0.774)$$

$$\therefore -\ln K = -2.05$$

$$\therefore K = e^{2.05} = 7.77$$

At this point, we write the equilibrium constant in terms of molar fractions,

$$\frac{y_{\text{H}_2\text{O}}^2 \times y_{\text{Cl}_2}^2}{y_{\text{O}_2} \times y_{\text{HCl}}^4} = \left( \frac{P}{P_0} \right)^{-\nu} K$$

The standard pressure  $P_0$  is 1 bar and, from the problem statement, the system pressure is 2 bar. Substituting these data, along with the expressions for the molar fractions obtained at the outset, we have

$$\frac{\left( \frac{2\varepsilon}{6-\varepsilon} \right)^2 \times \left( \frac{2\varepsilon}{6-\varepsilon} \right)^2}{\left( \frac{1-\varepsilon}{6-\varepsilon} \right) \times \left( \frac{5-4\varepsilon}{6-\varepsilon} \right)^4} = \left( \frac{2}{1} \right)^1 \times 7.77$$

$$\therefore \frac{\left( \frac{2\varepsilon}{6-\varepsilon} \right)^2 \times \left( \frac{2\varepsilon}{6-\varepsilon} \right)^2}{\left( \frac{1-\varepsilon}{6-\varepsilon} \right) \times \left( \frac{5-4\varepsilon}{6-\varepsilon} \right)^4} = 15.5$$

When expanded, the equation above is a fifth-degree polynomial in  $\varepsilon$ . One way to solve it is by dint of Mathematica's *Solve* function,

$$\text{Solve} \left[ \frac{\left( \frac{2\varepsilon}{6-\varepsilon} \right)^2 * \left( \frac{2\varepsilon}{6-\varepsilon} \right)^2}{\left( \frac{1-\varepsilon}{6-\varepsilon} \right) * \left( \frac{5-4\varepsilon}{6-\varepsilon} \right)^4} == 15.5, \varepsilon \right]$$

This returns four imaginary solutions and  $\varepsilon = 0.798$ , which is a viable result. Lastly, we can determine the equilibrium composition of the exit gases,

$$y_{\text{HCl}} = \frac{5-4\varepsilon}{6-\varepsilon} = \frac{5-4 \times 0.798}{6-0.798} = 0.348$$

$$y_{\text{O}_2} = \frac{1-\varepsilon}{6-\varepsilon} = \frac{1-0.798}{6-0.798} = 0.0388$$

$$y_{\text{H}_2\text{O}} = \frac{2\varepsilon}{6-\varepsilon} = \frac{2 \times 0.798}{6-0.798} = 0.307$$

$$y_{\text{Cl}_2} = y_{\text{H}_2\text{O}} = 0.307$$

Note that  $\sum y_i = 1$ , as it should be. The results are summarized below.

Component	Equilibrium molar fraction
HCl <sub>(g)</sub>	0.348
O <sub>2(g)</sub>	0.0388
H <sub>2</sub> O <sub>(g)</sub>	0.307
Cl <sub>2(g)</sub>	0.307

### P.3 → Solution

The initial number of moles and the stoichiometric coefficients are listed below.

Species ( <i>i</i> )	Initial No. of moles ( $n_{i,0}$ )	Stoichiometric c-efft ( $\nu_i$ )	$n_{i,0} + \nu_i \varepsilon$
N <sub>2</sub>	0.5	-0.5	0.5(1 - $\varepsilon$ )
H <sub>2</sub>	1.5	-1.5	1.5(1 - $\varepsilon$ )
NH <sub>3</sub>	0	1	$\varepsilon$
Total	2.0	-1	2 - $\varepsilon$

The molar fractions of each component are expressed in terms of the reaction coordinate  $\varepsilon$  as follows,

$$y_{N_2} = \frac{0.5 - 0.5\varepsilon}{2 - \varepsilon}$$

$$y_{H_2} = \frac{1.5 - 1.5\varepsilon}{2 - \varepsilon}$$

$$y_{NH_3} = \frac{\varepsilon}{2 - \varepsilon}$$

Equipped with these expressions, we state the equilibrium constant to be

$$\frac{y_{NH_3}}{y_{N_2}^{0.5} y_{H_2}^{1.5}} = K \left( \frac{P}{P_0} \right)^{-v} \rightarrow \frac{\left( \frac{\varepsilon}{2 - \varepsilon} \right)}{\left( \frac{0.5 - 0.5\varepsilon}{2 - \varepsilon} \right)^{0.5} \left( \frac{1.5 - 1.5\varepsilon}{2 - \varepsilon} \right)^{1.5}} = K \left( \frac{P}{P_0} \right)^{-(-1)}$$

$$\therefore \frac{\left( \frac{\varepsilon}{2 - \varepsilon} \right)}{\frac{0.5^{0.5} (1 - \varepsilon)^{0.5}}{(2 - \varepsilon)^{0.5}} \times \frac{1.5^{1.5} (1 - \varepsilon)^{1.5}}{(2 - \varepsilon)^{1.5}}} = K \left( \frac{P}{P_0} \right)$$

$$\therefore \frac{\left( \frac{\varepsilon}{2 - \varepsilon} \right)}{\frac{1.299 (1 - \varepsilon)^2}{(2 - \varepsilon)^2}} = K \left( \frac{P}{P_0} \right)$$

$$\therefore \frac{\varepsilon (2 - \varepsilon)}{(1 - \varepsilon)^2} = 1.299 K \left( \frac{P}{P_0} \right)$$

$$\therefore \frac{2\varepsilon - \varepsilon^2}{(1 - \varepsilon)^2} = 1.299 K \left( \frac{P}{P_0} \right)$$

Here, we multiply both sides by  $-1$ ,

$$\therefore \frac{\varepsilon^2 - 2\varepsilon}{(1 - \varepsilon)^2} = -1.299 K \left( \frac{P}{P_0} \right)$$

Then, we add and subtract 1 in the numerator of the right-hand side,

$$\therefore \frac{(\varepsilon^2 - 2\varepsilon + 1) - 1}{(1 - \varepsilon)^2} = -1.299 K \left( \frac{P}{P_0} \right)$$

$$\therefore \frac{(\varepsilon - 1)^2 - 1}{(1 - \varepsilon)^2} = -1.299 K \left( \frac{P}{P_0} \right)$$

Manipulating the left-hand side,

$$\therefore 1 - \frac{1}{(1 - \varepsilon)^2} = -1.299 K \left( \frac{P}{P_0} \right)$$

$$\therefore \frac{1}{(1 - \varepsilon)^2} = 1 + 1.299 K \left( \frac{P}{P_0} \right)$$

Modifying the exponents on each side,

$$(1 - \varepsilon)^2 = \left[ 1 + 1.299 K \left( \frac{P}{P_0} \right) \right]^{-1}$$

$$\therefore 1 - \varepsilon = \left[ 1 + 1.299 K \left( \frac{P}{P_0} \right) \right]^{-\frac{1}{2}}$$

At equilibrium,  $\varepsilon = \varepsilon_e$  and

$$1 - \varepsilon_e = \left[ 1 + 1.299K \left( \frac{P}{P_0} \right) \right]^{-\frac{1}{2}}$$

$$\therefore \varepsilon_e = 1 - \left[ 1 + 1.299K \left( \frac{P}{P_0} \right) \right]^{-\frac{1}{2}}$$

The relationship has been demonstrated.

### P.4 → Solution

To compute the equilibrium constant, we first require the change in Gibbs free energy,  $\Delta G$ . The heats of formation at 298 K of the three compounds in question, taken from Table 1, are listed below.

Compound	$\Delta H_f^\circ$ (J/mol)
C <sub>2</sub> H <sub>4</sub>	52,510
H <sub>2</sub> O	-241,818
C <sub>2</sub> H <sub>5</sub> OH	-235,100

The heat of reaction at 298 K is then

$$\Delta H_{298}^\circ = -235,100 - 52,510 - (-241,818) = -45,800 \text{ J/mol}$$

The Gibbs free energies of formation of the three compounds, also taken from Table 1, are listed below.

Compound	$\Delta G_f^\circ$ (J/mol)
C <sub>2</sub> H <sub>4</sub>	68,460
H <sub>2</sub> O	-228,572
C <sub>2</sub> H <sub>5</sub> OH	-168,490

The change in free energy at 298 K is then

$$\Delta G_{298}^\circ = -168,490 - 68,460 - (-228,572) = -8380 \text{ J/mol}$$

The heat capacity coefficients, taken from Table 2, are listed below.

Compound	A	B × 10 <sup>3</sup>	C × 10 <sup>6</sup>	D × 10 <sup>-5</sup>
C <sub>2</sub> H <sub>4</sub>	1.424	14.394	-4.392	-
H <sub>2</sub> O	3.470	1.450	-	0.121
C <sub>2</sub> H <sub>5</sub> OH	3.518	20.001	-6.002	-

Gleaning coefficients from the table above, we can calculate the  $\Delta$ 's.

$$\Delta A = 3.518 - 3.470 - 1.424 = -1.376$$

$$\Delta B = (20.001 - 1.450 - 14.394) \times 10^{-3} = 4.16 \times 10^{-3}$$

$$\Delta C = [-6.002 - 0 - (-4.392)] \times 10^{-6} = -1.61 \times 10^{-6}$$

$$\Delta D = (0 - 0.121 - 0) \times 10^5 = -1.21 \times 10^4$$

The temperature ratio is  $\tau = (200 + 273)/298 = 1.59$ . We proceed to evaluate the integrals

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \Delta A T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^2 (\tau^2 - 1) + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = -1.376 \times 298 \times (1.59 - 1) + \frac{4.16 \times 10^{-3}}{2} \times 298^2 \times (1.59^2 - 1) + (\dots)$$

$$(\dots) + \frac{(-1.61 \times 10^{-6})}{3} \times 298^3 \times (1.59^3 - 1) + \frac{(0.121 \times 10^5)}{298} \left( \frac{1.59 - 1}{1.59} \right) = -17.6$$

and

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = \Delta A \ln \tau + \left[ \Delta B T_0 + \left( \Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2} \right) \left( \frac{\tau + 1}{2} \right) \right] (\tau - 1)$$

$$\begin{aligned} \therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} &= 1.376 \times \ln(1.59) + (\dots) \\ (\dots) + \left\{ (4.16 \times 10^{-3}) \times 298 + \left[ (-1.61 \times 10^{-6}) \times 298^2 - \frac{1.21 \times 10^4}{1.59^2 \times 298^2} \right] \times \left( \frac{1.59+1}{2} \right) \right\} \times (1.59-1) \\ \therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} &= -0.0571 \end{aligned}$$

Substituting these and other data into the equation for  $\ln K$ , we get

$$\begin{aligned} -\ln K &= \frac{\Delta G_{298}^\circ - \Delta H_{298}^\circ}{RT_0} + \frac{\Delta H_{298}^\circ}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT - \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} \\ -\ln K &= \frac{-8380 - (-45,800)}{8.314 \times 298} + \frac{(-45,800)}{8.314 \times 473} + \frac{1}{473} \times (-17.6) - (-0.0571) = 3.48 \end{aligned}$$

Lastly,

$$K = \exp(-3.48) = \boxed{0.0308}$$

The equilibrium constant for this reaction at 200°C has been determined.

◆ The correct answer is **B**.

### P.5 → Solution

The number of moles initially present in the system is  $1 + 1.5 = 2.5$ . The stoichiometric coefficients of styrene, hydrogen, and ethylbenzene are  $-1$ ,  $-1$ , and  $1$ , respectively, and the stoichiometric coefficient of the reaction is  $\nu = -1 - 1 + 1 = -1$ . The number of moles of gas at equilibrium is  $n = n_0 + \nu \varepsilon = 2.5 - 1 \times \varepsilon = 2.5 - \varepsilon$ . The mole fractions of styrene, hydrogen, and ethylbenzene at equilibrium follow as

$$\begin{aligned} y_{C_6H_5CH=CH_2} &= \frac{(n_{sty})_0 + \nu_{sty} \varepsilon}{n} = \frac{1 - \varepsilon}{2.5 - \varepsilon} \\ y_{H_2} &= \frac{(n_{H_2})_0 + \nu_{H_2} \varepsilon}{n} = \frac{1.5 - \varepsilon}{2.5 - \varepsilon} \\ y_{C_6H_5C_2H_5} &= \frac{(n_{ebz})_0 + \nu_{ebz} \varepsilon}{n} = \frac{\varepsilon}{2.5 - \varepsilon} \end{aligned}$$

We can then write an expression for the equilibrium constant  $K$ ,

$$K = \frac{y_{C_6H_5C_2H_5}}{y_{C_6H_5CH=CH_2} y_{H_2}} = \frac{\left( \frac{\varepsilon}{2.5 - \varepsilon} \right)}{\left( \frac{1 - \varepsilon}{2.5 - \varepsilon} \right) \left( \frac{1.5 - \varepsilon}{2.5 - \varepsilon} \right)} = \frac{\varepsilon(2.5 - \varepsilon)}{(1 - \varepsilon)(1.5 - \varepsilon)} \quad (I)$$

To determine the composition of the system at equilibrium, we need the equilibrium constant  $K$ . This in turn requires the reaction change in Gibbs free energy  $\Delta G$ . The heats of formation at 298 K, taken from Table 1, are listed below.

Compound	$\Delta H_f^\circ$ (J/mol)
Styrene	147,360
Hydrogen	0
Ethylbenzene	29,920

The reaction  $\Delta H_{298}^\circ$  is, accordingly,

$$\Delta H_{298}^\circ = 29,920 - 0 - 147,360 = -117,400 \text{ kJ/mol}$$

The standard free energies of formation at 298 K, also taken from Table 1, are listed below.

Compound	$\Delta G_f^\circ$ (J/mol)
Styrene	213,900
Hydrogen	0
Ethylbenzene	130,890

The reaction  $\Delta G_{298}^{\circ}$  follows as

$$\Delta G_{298}^{\circ} = 130,890 - 0 - 213,900 = -83,000 \text{ J/mol}$$

The heat capacity coefficients for the three compounds in question, taken from Table 2, are listed below.

Compound	$A$	$B \times 10^3$	$C \times 10^6$	$D \times 10^{-5}$
Styrene	2.05	50.192	-16.662	-
Hydrogen	3.249	0.422	-	0.083
Ethylbenzene	1.124	55.380	-18.476	-

Then, we compute the coefficient variations  $\Delta A$ ,  $\Delta B$ ,  $\Delta C$  and  $\Delta D$ , namely

$$\Delta A = \Sigma(v_i A_i) = 1.0 \times 1.124 - (1.0 \times 2.05 + 1.0 \times 3.249)$$

$$\therefore \Delta A = -4.18$$

$$\Delta B = \Sigma(v_i B_i) = [(1.0 \times 55.38) - (1.0 \times 50.192 + 1.0 \times 0.422)] \times 10^{-3}$$

$$\therefore \Delta B = 4.77 \times 10^{-3}$$

$$\Delta C = \Sigma(v_i C_i) = [1.0 \times (-18.476) - 1.0 \times (-16.662)] \times 10^{-6}$$

$$\therefore \Delta C = -1.81 \times 10^{-6}$$

$$\Delta D = \Sigma(v_i D_i) = -0.083 \times 10^5$$

The temperature ratio is  $\tau = 923/298 = 3.10$ . Having established the  $\Delta$  coefficients, we can evaluate the heat capacity integrals

$$\int_{298}^{923} \frac{\Delta C_p^{\circ}}{R} dT = \Delta A T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^2 (\tau^2 - 1) + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right)$$

$$\therefore \int_{298}^{923} \frac{\Delta C_p^{\circ}}{R} dT = -4.18 \times 298 \times (3.10 - 1) + \frac{4.77 \times 10^{-3}}{2} \times 298^2 \times (3.1^2 - 1) + (\dots)$$

$$(\dots) + \frac{(-1.81 \times 10^{-6})}{3} \times 298^3 \times (3.10^3 - 1) + \frac{(-0.083 \times 10^5)}{298} \left( \frac{3.10 - 1}{3.10} \right) = -1270$$

and

$$\int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T} = \Delta A \ln \tau + \left[ \Delta B T_0 + \Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2} \left( \frac{\tau + 1}{2} \right) \right] (\tau - 1)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T} = -4.18 \times \ln 3.10 + \left[ (4.77 \times 10^{-3}) \times 298 + (-1.81 \times 10^{-6}) \times 298^2 + (\dots) \right] \times (3.10 - 1) = -2.12$$

We now have all the information needed to compute  $\ln K$ ,

$$-\ln K = \left( \frac{\Delta G_{298}^{\circ} - \Delta H_{298}^{\circ}}{RT_0} \right) + \frac{\Delta H_{298}^{\circ}}{RT_{923}} + \frac{1}{T_{923}} \int_{298}^{923} \frac{\Delta C_p^{\circ}}{R} dT - \int_{298}^{923} \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T}$$

$$\therefore -\ln K = \left[ \frac{-83,000 - (-117,400)}{8.314 \times 298} \right] + \frac{(-117,400)}{8.314 \times 923} + \frac{1}{923} \times (-1270) - (-2.12)$$

$$\therefore \ln K = 0.67$$

$$\therefore K = 1.95$$

Substituting  $K$  into equation (I) yields

$$\frac{\varepsilon(2.5 - \varepsilon)}{(1 - \varepsilon)(1.5 - \varepsilon)} = 1.95$$

This is a quadratic equation in  $\varepsilon$ ; solving it with a CAS such as Mathematica yields  $\varepsilon = 0.494$ . We can now determine the mole fraction composition of each component at equilibrium,

$$y_{\text{C}_6\text{H}_5\text{CH}=\text{CH}_2} = \frac{1 - 0.494}{2.5 - 0.494} = 0.252$$

$$y_{\text{H}_2} = \frac{1.5 - 0.494}{2.5 - 0.494} = 0.501$$

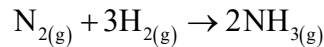
$$y_{\text{C}_6\text{H}_5\text{CH}=\text{CH}_2} = \frac{0.494}{2.5 - 0.494} = 0.246$$

The results are summarized below.

Component	Equilibrium molar fraction
$\text{C}_6\text{H}_5\text{CH}:\text{CH}_{2(\text{g})}$	0.252
$\text{H}_{2(\text{g})}$	0.501
$\text{C}_6\text{H}_5, \text{C}_2\text{H}_{5(\text{g})}$	0.246

## P.6 → Solution

**Part 1:** The reaction in question is of course

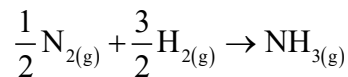


The only compound with a nonzero heat of formation is ammonia, for which  $\Delta H_f^\circ = -46,110 \text{ J/mol}$ . Accordingly,

$$\Delta H_{298}^\circ = 2\Delta H_f^\circ(\text{NH}_3) - \Delta H_f^\circ(\text{N}_2) - 3\Delta H_f^\circ(\text{H}_2)$$

$$\therefore \Delta H_{298}^\circ = 2 \times (-46,110) - 0 - 3 \times 0 = -92,200 \text{ J/mol}$$

Since the reaction we are concerned with is



it follows that  $\Delta H_{298}^\circ = -92,200/2 = -46,100 \text{ J/mol}$ . The reaction change in Gibbs free energy, given  $\Delta G_f^\circ$  values taken from Table 1, is

$$\Delta G_{298}^\circ = 2 \times (-16,400) - 0 - 3 \times 0 = -32,800 \text{ J/mol}$$

For the conditions in question,  $\Delta G_{298}^\circ = -32,800/2 = -16,400 \text{ J/mol}$ . The reaction is taking place at 300 K, not 298 K, and hence  $\Delta G$  will be slightly different from the foregoing result. The correct  $\Delta G$  can be found from the equation

$$\frac{\Delta G_{300}}{T_{300}} = \frac{\Delta G_{298}^\circ}{T_{298}} + \Delta H_{298}^\circ \left( \frac{1}{T_{300}} - \frac{1}{T_{298}} \right)$$

$$\therefore \frac{\Delta G_{300}}{300} = \frac{-16,400}{298} - 46,100 \times \left( \frac{1}{300} - \frac{1}{298} \right)$$

$$\therefore \Delta G_{300} = -16,200 \text{ J/mol}$$

Equipped with this result, we can determine the equilibrium constant  $K$ ,

$$\Delta G = -RT \ln K \rightarrow -16,200 = -8.314 \times 300 \ln K$$

$$\therefore K = 662$$

Normally, we'd apply this result in the law of mass action and solve the ensuing equation – usually an intricate polynomial – for the extent of reaction  $\varepsilon$ . However, in Problem 3 we derived a relation between  $K$  and  $\varepsilon_e$  for the ammonia synthesis reaction,

$$\varepsilon_e = 1 - \left( 1 + 1.299K \frac{P}{P_0} \right)^{-1/2}$$

Let us make use of this expression. Substituting the pertinent variables brings to

$$\varepsilon_e = 1 - \left( 1 + 1.299 \times 662 \times \frac{1.0}{1.0} \right)^{-1/2} = 0.966$$

The mole fraction of each component follows as

$$y_{\text{N}_2} = \frac{0.5 - 0.5\varepsilon}{2 - \varepsilon} = \frac{0.5 - 0.5 \times 0.966}{2 - 0.966} = 0.0164$$

$$y_{H_2} = \frac{1.5 - 1.5\varepsilon}{2 - \varepsilon} = \frac{1.5 - 1.5 \times 0.966}{2 - 0.966} = 0.0493$$

$$y_{NH_3} = \frac{\varepsilon}{2 - \varepsilon} = \frac{0.966}{2 - 0.966} = 0.934$$

The results are summarized below.

Component	Equilibrium molar fraction
N <sub>2(g)</sub>	0.0164
H <sub>2(g)</sub>	0.0493
NH <sub>3(g)</sub>	0.934

**Part 2:** Let the mole fraction of ammonia be 0.50. Solving for the extent of reaction  $\varepsilon$ , we obtain

$$y_{NH_3} = \frac{\varepsilon}{2 - \varepsilon} \rightarrow 0.5 = \frac{\varepsilon}{2 - \varepsilon}$$

$$\therefore \varepsilon = 0.667$$

Substituting in the  $\varepsilon$ - $K$  relation for ammonia synthesis, we get

$$0.667 = 1 - \left(1 + 1.299K \times \frac{1.0}{1.0}\right)^{-0.5} \rightarrow K = 6.17$$

The temperature at which  $K = 6.17$  can be obtained with the relation

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \rightarrow \ln\left(\frac{6.17}{662}\right) = -\frac{(-46,100)}{8.314}\left(\frac{1}{T} - \frac{1}{300}\right)$$

$$\therefore \boxed{T = 402 \text{ K}}$$

◆ The correct answer is **B**.

**Part 3:** As established in the previous part, the extent of reaction for a 0.50 mole fraction of ammonia is  $\varepsilon = 0.667$ . Substituting in the  $\varepsilon$ - $K$  relation and solving for  $K$ , we get

$$0.667 = 1 - \left(1 + 1.299 \times K \times \frac{100}{1}\right)^{-0.5} \rightarrow K = 0.0617$$

The temperature that corresponds to this equilibrium constant is found as

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \rightarrow \ln\left(\frac{0.0617}{662}\right) = -\frac{(-46,100)}{8.314}\left(\frac{1}{T} - \frac{1}{300}\right)$$

$$\therefore \boxed{T = 603 \text{ K}}$$

◆ The correct answer is **A**.

## P.7 → Solution

The molar fractions of each component are

$$y_{N_2O_4} = \frac{1 - \varepsilon}{1 + \varepsilon}$$

$$y_{NO_2} = \frac{2\varepsilon}{1 + \varepsilon}$$

The heat of reaction at 298 K, given the  $\Delta H_f^\circ$  values from Table 1, is

$$\Delta H_{298}^\circ = 2 \times 33,180 - 9160 = 57,200 \text{ J/mol}$$

Likewise,  $\Delta G_{298}$  is given by

$$\Delta G_{298}^\circ = 2 \times 51,310 - 97,540 = 5080 \text{ J/mol}$$

The heat-capacity equation parameters, taken from Table 2, are listed below.

Compound	A	B × 10 <sup>3</sup>	C × 10 <sup>6</sup>	D × 10 <sup>-5</sup>
N <sub>2</sub> O <sub>4</sub>	11.66	2.257	–	–2.787
NO <sub>2</sub>	4.982	1.195	–	–0.792

The Δ terms are calculated next,

$$\Delta A = 2 \times 4.982 - 11.66 = -1.70$$

$$\Delta B = (2 \times 1.195 - 2.257) \times 10^{-3} = 1.33 \times 10^{-4}$$

$$\Delta C = 0$$

$$\Delta D = [2 \times (-0.792) - (-2.787)] \times 10^5 = 1.20 \times 10^5$$

The temperature ratio is  $\tau = 350/298 = 1.17$ . We proceed to evaluate the integrals

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \Delta A T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^2 (\tau^2 - 1) + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = -1.70 \times 298 \times (1.17 - 1) + \frac{1.33 \times 10^{-4}}{2} \times 298^2 \times (1.17^2 - 1) + 0 + \frac{1.20 \times 10^5}{298} \times \left( \frac{1.17 - 1}{1.17} \right)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = -25.4$$

and

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = \Delta A \ln \tau + \left[ \Delta B T_0 + \left( \Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2} \right) \left( \frac{\tau + 1}{2} \right) \right] (\tau - 1)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = -1.70 \times \ln(1.17) + \left[ (1.33 \times 10^{-4}) \times 298 + \left( 0 + \frac{1.20 \times 10^5}{1.17^2 \times 298^2} \right) \times \left( \frac{1.17 + 1}{2} \right) \right] \times (1.17 - 1)$$

$$\therefore \therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = -0.0781$$

so that

$$-\ln K = \frac{\Delta G_{298}^\circ - \Delta H_{298}^\circ}{RT_0} + \frac{\Delta H_{298}^\circ}{RT} + \frac{1}{T} \int_{298}^{300} \frac{\Delta C_p^\circ}{R} dT - \int_{298}^{300} \frac{\Delta C_p^\circ}{R} \frac{dT}{T}$$

$$\therefore -\ln K = \frac{5080 - 57,200}{8.314 \times 298} + \frac{57,200}{8.314 \times 350} + \frac{1}{350} \times (-25.4) - (-0.0781) = -1.37$$

$$\therefore K = e^{1.37} = 3.93$$

From the law of mass action,

$$\frac{(2\varepsilon)^2}{(1-\varepsilon)(1+\varepsilon)} = \left( \frac{P}{P_0} \right)^{-1} K$$

$$\therefore \frac{(2\varepsilon)^2}{(1-\varepsilon)(1+\varepsilon)} = \left( \frac{5.0}{1.0} \right)^{-1} \times 3.93$$

Solving the equation above yields  $\varepsilon = 0.405$ . Accordingly, the equilibrium mole fractions of N<sub>2</sub>O<sub>4</sub> and NO<sub>2</sub> are, respectively,

$$y_{\text{N}_2\text{O}_4} = \frac{1-\varepsilon}{1+\varepsilon} = \frac{1-0.405}{1+0.405} = 0.423$$

$$y_{\text{NO}_2} = \frac{2 \times 0.405}{1+0.405} = 0.577$$

Component	Equilibrium molar fraction
N <sub>2</sub> O <sub>4(g)</sub>	0.423
NO <sub>2(g)</sub>	0.577



### P.8 → Solution

The molar fractions of each component are

$$y_{CO_2} = \frac{1 - \varepsilon}{3 - 2\varepsilon}$$

$$y_{H_2} = \frac{2 - 2\varepsilon}{3 - 2\varepsilon}$$

$$y_{CH_3OH} = \frac{\varepsilon}{3 - 2\varepsilon}$$

The heat of reaction at 298 K, given the  $\Delta H_f^\circ$  values from Table 1, is

$$\Delta H_{298}^\circ = -200,660 - (-110,525) = -90,100 \text{ J/mol}$$

Likewise,  $\Delta G_{298}$  is given by

$$\Delta G_{298}^\circ = -161,960 - (-137,169) = -24,800 \text{ J/mol}$$

The heat-capacity equation coefficients, taken from Table 2, are listed below.

Compound	A	B × 10 <sup>3</sup>	C × 10 <sup>6</sup>	D × 10 <sup>-5</sup>
CH <sub>3</sub> OH	2.211	12.216	-3.450	0
CO	3.376	0.557	0	-0.031
H <sub>2</sub>	3.249	0.422	0	0.083

The  $\Delta$  terms are calculated next,

$$\Delta A = 1 \times 2.211 + (-1) \times 3.376 + (-2) \times 3.249 = -7.66$$

$$\Delta B = [1 \times 12.216 + (-1) \times 0.557 + (-2) \times 0.422] \times 10^{-3} = 0.0108$$

$$\Delta C = -3.45 \times 10^{-6}$$

$$\Delta D = [1 \times 0 + (-1) \times (-0.031) + (-2) \times 0.083] \times 10^5 = -1.35 \times 10^4$$

The temperature ratio is  $\tau = 300/298 = 1.01$ . We proceed to evaluate the integrals

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \Delta A T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^2 (\tau^2 - 1) + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = -7.66 \times 298 \times (1.01 - 1) + \frac{0.0108}{2} \times 298^2 \times (1.01^2 - 1) - (\dots)$$

$$(\dots) - \frac{(3.45 \times 10^{-6})}{3} \times 298^3 \times (1.01^3 - 1) - \frac{(1.35 \times 10^4)}{298} \times \left( \frac{1.01 - 1}{1.01} \right) = -14.6$$

and

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = \Delta A \ln \tau + \left[ \Delta B T_0 + \left( \Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2} \right) \left( \frac{\tau + 1}{2} \right) \right] (\tau - 1)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = -7.66 \ln 1.01 + (\dots)$$

$$(\dots) + \left\{ 0.0108 \times 298 + \left[ (-3.45 \times 10^{-6}) \times 298^2 - \frac{1.35 \times 10^4}{1.01^2 \times 298^2} \right] \times \left( \frac{1.01 + 1}{2} \right) \right\} \times (1.01 - 1) = -0.0486$$

so that

$$-\ln K = \frac{\Delta G_{298}^\circ - \Delta H_{298}^\circ}{RT_0} + \frac{\Delta H_{298}^\circ}{RT} + \frac{1}{T} \int_{298}^{300} \frac{\Delta C_p^\circ}{R} dT - \int_{298}^{300} \frac{\Delta C_p^\circ}{R} \frac{dT}{T}$$

$$\therefore -\ln K = \frac{-24,800 - (-90,100)}{8.314 \times 298} + \frac{(-90,100)}{8.314 \times 300} + \frac{1}{300} \times (-14.6) - (-0.0486) = -9.75$$

$$K = e^{9.75} = 17,100$$

From the law of mass action,

$$\frac{\varepsilon(3-2\varepsilon)^2}{4(1-\varepsilon)^3} = \left(\frac{P}{P_0}\right)^2 K = 1.0 \times 17,100$$

Solving the equation above yields  $\varepsilon = 0.975$ . Accordingly, the equilibrium mole fractions of each component are listed below.

$$y_{\text{CO}_2} = \frac{1-0.975}{3-2 \times 0.975} = 0.0238$$

$$y_{\text{H}_2} = \frac{2-2 \times 0.975}{3-2 \times 0.975} = 0.0476$$

$$y_{\text{CH}_3\text{OH}} = \frac{0.975}{3-2 \times 0.975} = 0.929$$

The results are summarized in the following table.

Component	Equilibrium molar fraction
CO <sub>2(g)</sub>	0.0238
H <sub>2(g)</sub>	0.0476
CH <sub>3OH(g)</sub>	0.929

### P.9 → Solution

The molar fractions of each component are

$$y_{\text{N}_2} = \frac{1-\varepsilon}{2}$$

$$y_{\text{C}_2\text{H}_2} = \frac{1-\varepsilon}{2}$$

$$y_{\text{HCN}} = \frac{2\varepsilon}{2} = \varepsilon$$

The heat of reaction at 298 K, given the  $\Delta H_f^\circ$  values from Table 1, is

$$\Delta H_{298}^\circ = 2 \times 135,100 - 1 \times 0 - 1 \times 227,480 = 42,700 \text{ J/mol}$$

Similarly,  $\Delta G_{298}^\circ$  is given by

$$\Delta G_{298}^\circ = 2 \times 124,700 - 1 \times 0 - 1 \times 209,970 = 39,400 \text{ J/mol}$$

The heat-capacity equation parameters, taken from Table 2, are listed below.

Compound	A	B × 10 <sup>3</sup>	C × 10 <sup>6</sup>	D × 10 <sup>-5</sup>
N <sub>2</sub>	3.280	0.593	–	0.040
C <sub>2</sub> H <sub>2</sub>	6.132	1.952	–	-1.299
HCN	4.736	1.359	–	-0.725

The  $\Delta$  terms are calculated next,

$$\Delta A = 2 \times 4.736 - 1 \times 3.280 - 1 \times 6.132 = 0.06$$

$$\Delta B = (2 \times 1.359 - 1 \times 0.593 - 1 \times 1.952) \times 10^{-3} = 1.73 \times 10^{-4}$$

$$\Delta C = 0$$

$$\Delta D = [2 \times (-0.725) - 1 \times 0.04 - 1 \times (-1.299)] \times 10^5 = -1.91 \times 10^4$$

The temperature ratio is  $\tau = 923/298 = 3.10$ . We proceed to evaluate the integrals

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \Delta A T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^2 (\tau^2 - 1) + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = 0.06 \times 298 \times (3.10 - 1) + \frac{1.73 \times 10^{-4}}{2} \times 298^2 \times (3.10^2 - 1) + 0 - \frac{1.91 \times 10^4}{298} \times \left( \frac{3.10 - 1}{3.10} \right)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = 60.3$$

and

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = \Delta A \ln \tau + \left[ \Delta B T_0 + \left( \Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2} \right) \left( \frac{\tau+1}{2} \right) \right] (\tau-1)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = 0.06 \times \ln(3.10) + \left\{ (1.73 \times 10^{-4}) \times 298 + \left[ 0 - \frac{1.91 \times 10^4}{3.10^2 \times 298^2} \right] \times \left( \frac{3.10+1}{2} \right) \right\} \times (3.10-1)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = 0.0798$$

so that

$$-\ln K = \frac{\Delta G_{298}^\circ - \Delta H_{298}^\circ}{RT_0} + \frac{\Delta H_{298}^\circ}{RT} + \frac{1}{T} \int_{298}^{300} \frac{\Delta C_p^\circ}{R} dT - \int_{298}^{300} \frac{\Delta C_p^\circ}{R} \frac{dT}{T}$$

$$\therefore -\ln K = \frac{39,400 - 42,700}{8.314 \times 298} + \frac{42,700}{8.314 \times 923} + \frac{1}{923} \times 60.3 - 0.0798 = 4.22$$

$$\therefore K = e^{-4.22} = 0.0147$$

From the law of mass action,

$$\left( \frac{2\varepsilon}{1-\varepsilon} \right)^2 = K = 0.0147$$

Solving the equation above yields  $\varepsilon = 0.0572$ . Accordingly, the equilibrium mole fractions of nitrogen, acetylene, and hydrogen cyanide are, respectively,

$$y_{N_2} = \frac{1-\varepsilon}{2} = \frac{1-0.0572}{2} = 0.471$$

$$y_{C_2H_2} = y_{N_2} = 0.471$$

$$y_{HCN} = \varepsilon = 0.0572$$

The results are summarized in the following table.

Component	Equilibrium molar fraction
N <sub>2(g)</sub>	0.471
C <sub>2</sub> H <sub>2(g)</sub>	0.471
HCN <sub>(g)</sub>	0.0572

### P.10 → Solution

The carbon exists pure as an individual phase, for which the activity is unity. Thus, we leave it out of consideration. The mole fractions of the other two components are

$$y_{CH_4} = \frac{1-\varepsilon}{1+\varepsilon}$$

$$y_{H_2} = \frac{2\varepsilon}{1+\varepsilon}$$

The heat of reaction at 298 K, given the  $\Delta H_f^\circ$  values from Table 1, is

$$\Delta H_{298}^\circ = 1 \times 0 + 2 \times 0 - (-74,520) = 74,500 \text{ J/mol}$$

Similarly,  $\Delta G_{298}$  is given by

$$\Delta G_{298}^\circ = 1 \times 0 + 2 \times 0 - (-50,460) = 50,500 \text{ J/mol}$$

The heat-capacity equation parameters, taken from Table 2, are listed below.

Compound	A	B × 10 <sup>3</sup>	C × 10 <sup>6</sup>	D × 10 <sup>-5</sup>
CH <sub>4</sub>	1.702	9.081	-2.164	-
C <sub>(s)</sub>	1.771	0.771	-	-0.867
H <sub>2</sub>	3.249	0.422	-	0.083

The Δ terms are calculated next,

$$\Delta A = 2 \times 3.249 + 1 \times 1.771 - 1.702 = 6.57$$

$$\Delta B = (2 \times 0.422 + 1 \times 0.771 - 1 \times 9.081) \times 10^{-3} = -7.47 \times 10^{-3}$$

$$\Delta C = [2 \times 0 + 1 \times 0 - 1 \times (-2.164)] \times 10^{-6} = 2.16 \times 10^{-6}$$

$$\Delta D = [2 \times 0.083 + 1 \times (-0.867) - 1 \times 0] \times 10^5 = -7.01 \times 10^4$$

The temperature ratio is  $\tau = 923/298 = 3.10$ . We proceed to evaluate the integrals

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \Delta A T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^2 (\tau^2 - 1) + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right)$$

$$\begin{aligned} \therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT &= 6.57 \times 298 \times (3.10 - 1) - \frac{7.47 \times 10^{-3}}{2} \times 298^2 \times (3.10^2 - 1) + (\dots) \\ &(\dots) + \frac{2.16 \times 10^{-6}}{3} \times 298^3 \times (3.10^3 - 1) - \frac{7.01 \times 10^4}{298} \times \left( \frac{3.10 - 1}{3.10} \right) \end{aligned}$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = 1645$$

and

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = \Delta A \ln \tau + \left[ \Delta B T_0 + \left( \Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2} \right) \left( \frac{\tau + 1}{2} \right) \right] (\tau - 1)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = 6.57 \times \ln(3.10) + (\dots)$$

$$(\dots) + \left\{ (-7.47 \times 10^{-3}) \times 298 + \left[ (2.16 \times 10^{-6}) \times 298^2 - \frac{7.01 \times 10^4}{3.10^2 \times 298^2} \right] \times \left( \frac{3.10 + 1}{2} \right) \right\} \times (3.10 - 1)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = 3.23$$

so that

$$-\ln K = \frac{\Delta G_{298}^\circ - \Delta H_{298}^\circ}{RT_0} + \frac{\Delta H_{298}^\circ}{RT} + \frac{1}{T} \int_{298}^{300} \frac{\Delta C_p^\circ}{R} dT - \int_{298}^{300} \frac{\Delta C_p^\circ}{R} \frac{dT}{T}$$

$$\therefore -\ln K = \frac{50,500 - 74,500}{8.314 \times 298} + \frac{74,500}{8.314 \times 923} + \frac{1}{923} \times 1645 - 3.23 = -1.43$$

$$\therefore K = e^{1.43} = 4.18$$

From the law of mass action,

$$\frac{(2\varepsilon)^2}{(1+\varepsilon)(1-\varepsilon)} = \left( \frac{P}{P_0} \right)^{-1} K$$

$$\therefore \frac{(2\varepsilon)^2}{(1-\varepsilon)(1+\varepsilon)} = 1 \times 4.18 = 4.18$$

Solving the equation above yields  $\varepsilon = 0.715$ . Accordingly, the equilibrium mole fractions of methane and hydrogen are, respectively,

$$y_{\text{CH}_4} = \frac{1-\varepsilon}{1+\varepsilon} = \frac{1-0.715}{1+0.715} = 0.166$$

$$y_{\text{H}_2} = \frac{2 \times 0.715}{1+0.715} = 0.834$$

The results are summarized in the following table.

Component	Equilibrium molar fraction
CH <sub>4(g)</sub>	0.166
H <sub>2(g)</sub>	0.834

### P.11 → Solution

The sulfur exists pure as a solid phase, for which the activity is  $f/f_0$ . Since  $f$  and  $f_0$  are for practical purposes the same, the activity is unity, and it is omitted from the equilibrium equation. The molar fractions of each component are

$$y_{H_2S} = \frac{2-2\varepsilon}{3-\varepsilon}$$

$$y_{SO_2} = \frac{1-\varepsilon}{3-\varepsilon}$$

$$y_{H_2O} = \frac{2\varepsilon}{3-\varepsilon}$$

The heat of reaction at 298 K, given the  $\Delta H_f^\circ$  values from Table 1, is

$$\Delta H_{298}^\circ = 2 \times (-241,818) - 2 \times (-20,630) - (-296,830) = -146,000 \text{ J/mol}$$

Likewise,  $\Delta G_{298}^\circ$  is given by

$$\Delta G_{298}^\circ = 2 \times (-228,572) - 2 \times (-33,560) - (-300,194) = -89,800 \text{ J/mol}$$

The heat-capacity equation parameters, taken from Table 2, are listed below.

Compound	A	B × 10 <sup>3</sup>	C × 10 <sup>6</sup>	D × 10 <sup>-5</sup>
H <sub>2</sub> S	3.931	1.490	–	–0.232
SO <sub>2</sub>	5.699	0.801	–	–1.015
S <sub>(s)</sub>	4.114	–1.728	–	–0.783
H <sub>2</sub> O	3.470	1.450	–	0.121

The  $\Delta$  terms are calculated next,

$$\Delta A = 2 \times 3.470 + 3 \times 4.114 - 2 \times 3.931 - 1 \times 5.699 = 5.72$$

$$\Delta B = [2 \times 1.490 + 3 \times (-1.728) - 2 \times 1.450 - 1 \times 0.801] \times 10^{-3} = -5.99 \times 10^{-3}$$

$$\Delta C = 0$$

$$\Delta D = [2 \times 0.121 + 3 \times (-0.783) - 2 \times (-0.232) - 1 \times (-1.015)] \times 10^5 = -6.28 \times 10^4$$

The temperature ratio is  $\tau = 723/298 = 2.43$ . We proceed to evaluate the integrals

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = \Delta A T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^2 (\tau^2 - 1) + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = 5.72 \times 298 \times (2.43 - 1) - \frac{5.99 \times 10^{-3}}{2} \times 298^2 \times (2.43^2 - 1) + 0 - \frac{6.28 \times 10^4}{298} \times \left( \frac{2.43 - 1}{2.43} \right)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT = 1010$$

and

$$\int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = \Delta A \ln \tau + \left[ \Delta B T_0 + \left( \Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2} \right) \left( \frac{\tau + 1}{2} \right) \right] (\tau - 1)$$

$$\therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = 5.72 \times \ln(2.43) + \left[ (-5.99 \times 10^{-3}) \times 298 + \left( 0 - \frac{6.28 \times 10^4}{2.43^2 \times 298^2} \right) \times \left( \frac{2.43 + 1}{2} \right) \right] \times (2.43 - 1)$$

$$\therefore \therefore \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} = 2.23$$

so that

$$-\ln K = \frac{\Delta G_{298}^{\circ} - \Delta H_{298}^{\circ}}{RT_0} + \frac{\Delta H_{298}^{\circ}}{RT} + \frac{1}{T} \int_{298}^{300} \frac{\Delta C_p^{\circ}}{R} dT - \int_{298}^{300} \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T}$$

$$\therefore -\ln K = \frac{-89,800 - (-146,000)}{8.314 \times 298} - \frac{146,000}{8.314 \times 723} + \frac{1}{723} \times 1010 - 2.23 = -2.44$$

$$\therefore K = e^{2.44} = 11.5$$

From the law of mass action,

$$\frac{(2\varepsilon)^2(3-\varepsilon)}{(2-2\varepsilon)^2(1-\varepsilon)} = \left(\frac{P}{P_0}\right)^1 K = \left(\frac{8}{1}\right) \times 11.5 = 92$$

Solving the equation above yields  $\varepsilon = 0.759$ . Accordingly, the equilibrium mole fractions of  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{O}$  are, respectively,

$$y_{\text{H}_2\text{S}} = \frac{2-2\varepsilon}{3-\varepsilon} = \frac{2-2 \times 0.759}{3-0.759} = 0.215$$

$$y_{\text{SO}_2} = \frac{1-\varepsilon}{3-\varepsilon} = \frac{1-0.759}{3-0.759} = 0.108$$

$$y_{\text{H}_2\text{O}} = \frac{2 \times 0.759}{3-0.759} = 0.677$$

The results are summarized below.

Component	Equilibrium molar fraction
$\text{H}_2\text{S}_{(\text{g})}$	0.215
$\text{SO}_{2(\text{g})}$	0.108
$\text{H}_2\text{O}_{(\text{g})}$	0.677

## ► REFERENCES

- SMITH, J., VAN NESS, H., and ABBOTT, M. (2004). *Introduction to Chemical Engineering Thermodynamics*. 7th edition. New York: McGraw-Hill.



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