

(*This assignment is *optional*. You lose no marks if you don't hand it in.)

1. The logarithm of the equilibrium constant of the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$ at different temperatures is

T / K	$\ln K$
298.15	-13.205
500.00	2.309
1000.00	14.892
2000.00	21.582

[10]

- Prepare a van't Hoff graph by plotting $\ln K$ against $1/T$.
- Is the slope $-\Delta H^\circ/R$ independent of temperature? Is ΔH° for the reaction constant? Explain.
- Calculate ΔG° , ΔH° and ΔS° at 1000 K. (*Suggestion*: Use $\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$)
- Use the van't Hoff graph to calculate $\ln K$ at 700 K.
- Why is the chemical equilibrium of N_2 , H_2 and NH_3 of "huge" practical significance?

2. Pure ammonia initially at 2.00 bar and 500 K partially decomposes to nitrogen and hydrogen at constant temperature and pressure. Using data provided for Question 1, calculate the percentage of ammonia that decomposes under these conditions.

[3]

3. This question refers to the multiphase equilibrium for the decomposition of calcium carbonate to form calcium oxide and carbon dioxide gas:

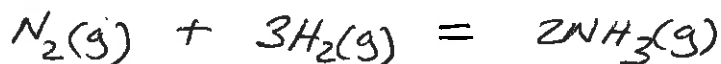


Data at 25° C: $\Delta H_{\text{fm}}^\circ(\text{CaCO}_3, \text{s}) = -1206.92 \text{ kJ mol}^{-1}$ $\Delta G_{\text{fm}}^\circ(\text{CaCO}_3, \text{s}) = -1128.79 \text{ kJ mol}^{-1}$
 $\Delta H_{\text{fm}}^\circ(\text{CaO}, \text{s}) = -635.09 \text{ kJ mol}^{-1}$ $\Delta G_{\text{fm}}^\circ(\text{CaO}, \text{s}) = -604.03 \text{ kJ mol}^{-1}$
 $\Delta H_{\text{fm}}^\circ(\text{CO}_2, \text{g}) = -393.509 \text{ kJ mol}^{-1}$ $\Delta G_{\text{fm}}^\circ(\text{CO}_2, \text{g}) = -394.359 \text{ kJ mol}^{-1}$

[7]

- Calculate the equilibrium constant $K = p_{\text{CO}_2}/p^\circ$ for the reaction at 25 °C.
- Calculate the standard enthalpy change of the reaction at 25 °C.
- Estimate the decomposition temperature of $\text{CaCO}_3(\text{s})$ at 1.00 bar. (*Suggestion*: Use the van't Hoff equation to calculate the temperature at which $p_{\text{CO}_2} = 1 \text{ bar}$.)
- Why is the decomposition temperature of $\text{CaCO}_3(\text{s})$ of "huge" practical significance?

(Q1)



a) see Graph A van't Hoff plot $\ln K$ vs $\frac{1}{T}$

linear equation $\ln K = a_0 + a_1 \frac{1}{T}$ fitted to the data

$a_0 = \text{intercept}$

$a_1 = \text{slope}$

regression gives
($r^2 = 0.99900$)

$$a_0 = 27.2291$$

$$a_1 = -12159.0 \text{ K}$$

see Graph B van't Hoff plot $\ln K$ vs $\frac{1}{T}$

quadratic equation: $\ln K = a_0 + a_1 \frac{1}{T} + a_2 \left(\frac{1}{T}\right)^2$
fitted to the data

$$a_0 = 28.4890$$

$$a_1 = -14073.6 \text{ K}$$

$$a_2 = 489879 \text{ K}^2$$

$$(r^2 = 0.99999)$$

b) Is the plot of $\ln K$ against $\frac{1}{T}$ linear?
Is ΔH° constant?

almost!

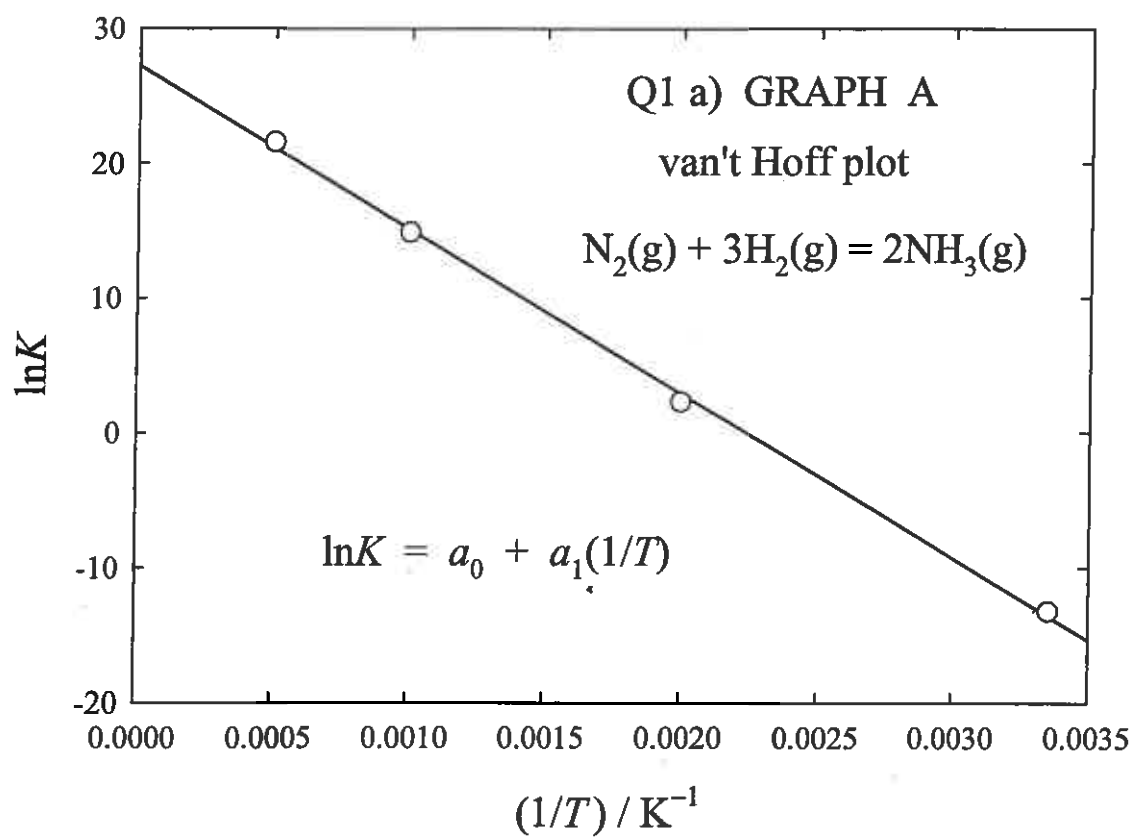
Graph A with fitting equation

slight curvature indicated

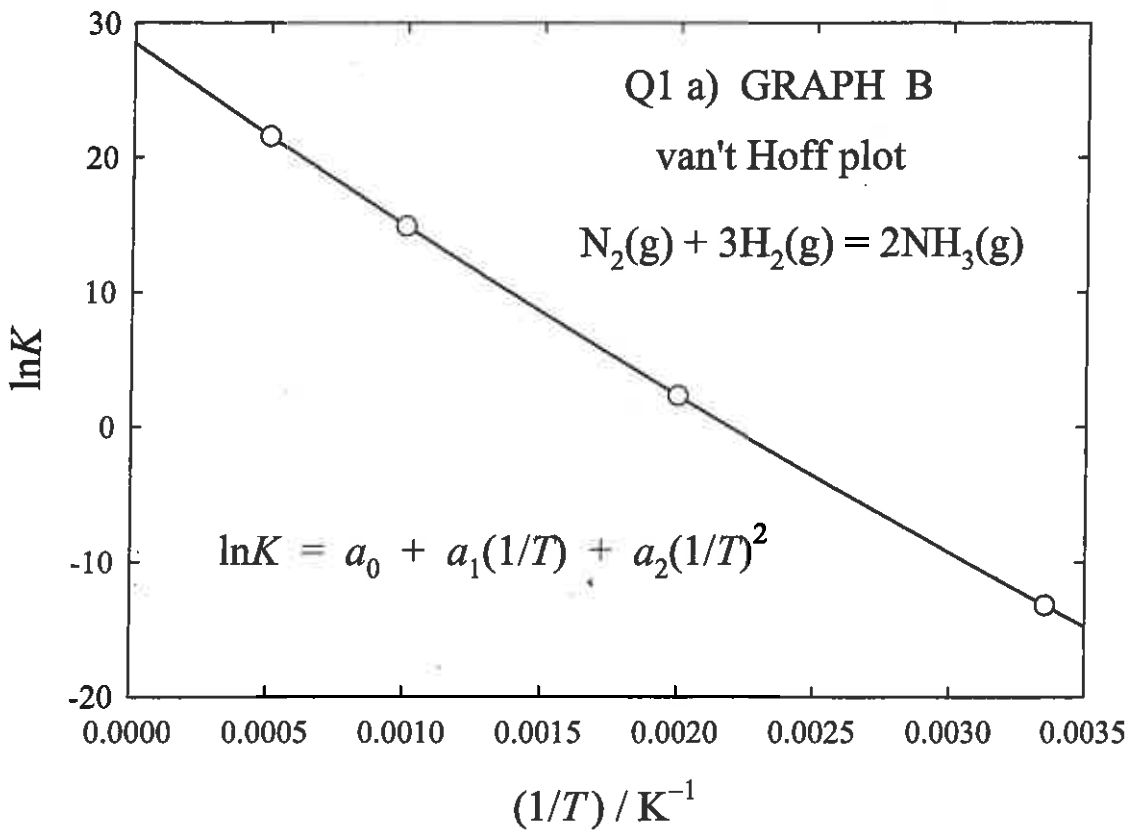
$a_0 + a_1 \frac{1}{T}$ gives a good description of the data

But... Graph B with quadratic fitting equation

$a_0 + a_1 \left(\frac{1}{T}\right) + a_2 \left(\frac{1}{T}\right)^2$ goes "right through" all the data points



better:



(Q1 cont.)

c) calculate ΔG° , ΔH° , ΔS° at 1000 K

Using Graph A
(linear fitting equation) slope $\frac{d \ln K}{d \frac{1}{T}} = \text{constant} = a_1 = -12159.0 \text{ K}$

$$\Delta H^\circ = \frac{d \ln K}{d \frac{1}{T}} = -\frac{\Delta H^\circ}{R} \Rightarrow \Delta H^\circ = -R \frac{d \ln K}{d \frac{1}{T}}$$

$$\Delta H^\circ = -R a_1 = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(-12159.0 \text{ K})$$

$$\Delta H^\circ = 101,100 \text{ J mol}^{-1} = 101.1 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(1000 \text{ K})(14.892)$$

$$\Delta G^\circ = -123,800 \text{ J mol}^{-1} = -123.8 \text{ kJ}$$

$$\Delta G^\circ = \Delta(H^\circ - TS^\circ) \stackrel{(T \text{ const.})}{=} \Delta H^\circ - \Delta(TS^\circ) = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{101,100 - (-123,800)}{1000} = 224.9 \frac{\text{J}}{\text{K mol}^{-1}}$$

Using Graph B (slightly more accurate)

allows for slight curvature of $\ln K$ vs $\frac{1}{T}$ plot

$$\text{slope at } 1000 \text{ K} \quad \frac{d \ln K}{d \frac{1}{T}} = \frac{d}{d \frac{1}{T}} \left[a_0 + a_1 \frac{1}{T} + a_2 \left(\frac{1}{T} \right)^2 \right] = a_1 + 2a_2 \frac{1}{T}$$

$$= -14073.6 + 2(489879) \frac{1}{1000} = -13094 \text{ K}$$

$$\Delta H^\circ = -R \frac{d \ln K}{d \frac{1}{T}} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(-13094 \text{ K}) = 108,900 \frac{\text{J}}{\text{mol}}$$

$$\Delta S^\circ \quad \Delta G^\circ = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(1000 \text{ K})(14.892) = -123800 \frac{\text{J}}{\text{mol}}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{108,900 - (-123,800)}{1000} = 232.7 \frac{\text{J}}{\text{K mol}}$$

(Q1 cont.)

d) value of equilibrium constant at $T = 700 \text{ K}$?

Graph A $\ln K = a_0 + a_1 \frac{1}{T} = 27.2291 - 12159.0 \frac{1}{700}$
 $\ln K = 9.8591 \quad K = e^{9.8591} = 19,130$

Graph B (more accurate) $\ln K = a_0 + a_1 \frac{1}{T} + a_2 \left(\frac{1}{T}\right)^2 = 28.4890 - \frac{14073.6}{700} + \frac{489877}{700^2}$
 $\ln K = 9.3836 \quad K = e^{9.3836} = 11,890$

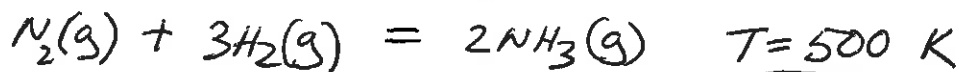
e) why is the $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$

of practical significance?

industrial production of NH_3 (≈ 200 million tons per year)
 \Rightarrow "billion"-dollar business

essential for agricultural fertilizers and food production,
and the synthesis of nitrogen compounds
(acrylonitrile, urea, ammonium nitrate, HCN , ...)

Q2



$$K = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = e^{2.309} = 10.06$$

$$\ln K = 2.309 \quad (\text{from Q1})$$

$$\text{total pressure } p = 2.00 \text{ bar}$$

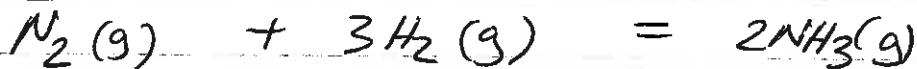
$$= P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3}$$

(Q2 cont.)

Suggestion: start with: 1.00 mol pure NH_3

to reach equilibrium, ϵ moles of NH_3 decomposes

from stoichiometry:



moles initially: 0 0 1.00 mol

moles at
at equilibrium: $\frac{\epsilon}{2}$ $\frac{3\epsilon}{2}$ $1.00 - \epsilon$

$$\frac{P_{\text{NH}_3}}{P} = \text{mole fraction } \text{NH}_3 = \frac{1 - \epsilon}{1 - \epsilon + \frac{\epsilon}{2} + \frac{3\epsilon}{2}} = \frac{n_{\text{NH}_3}}{n_{\text{N}_2} + n_{\text{H}_2} + n_{\text{NH}_3}}$$

$$\frac{P_{\text{NH}_3}}{P} = \frac{1 - \epsilon}{1 + \epsilon}$$

$$\frac{P_{\text{N}_2}}{P} = \text{mole fraction } \text{N}_2 = \frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{H}_2} + n_{\text{NH}_3}} = \frac{\epsilon/2}{1 - \epsilon + \frac{\epsilon}{2} + \frac{3\epsilon}{2}} = \frac{\epsilon/2}{1 + \epsilon}$$

$$\frac{P_{\text{H}_2}}{P} = \text{mole fraction } \text{H}_2 = \frac{n_{\text{H}_2}}{n_{\text{N}_2} + n_{\text{H}_2} + n_{\text{NH}_3}} = \frac{\frac{3\epsilon}{2}}{1 + \epsilon}$$

$$K = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

$$\left\{ \begin{array}{l} P_{\text{NH}_3} = \frac{1 - \epsilon}{1 + \epsilon} P \\ P_{\text{N}_2} = \frac{\epsilon/2}{1 + \epsilon} P \\ P_{\text{H}_2} = \frac{3\epsilon/2}{1 + \epsilon} P \end{array} \right.$$

$$\boxed{\begin{array}{l} p = \text{total pressure} \\ = 2.00 \text{ bar} \end{array}}$$

$$K = \frac{\left(\frac{1 - \epsilon}{1 + \epsilon} P\right)^2}{\left(\frac{1}{2} \frac{\epsilon}{1 + \epsilon} P\right) \left(\frac{3}{2} \frac{\epsilon}{1 + \epsilon} P\right)^3} = \frac{(1 - \epsilon)^2}{\epsilon(\epsilon^3)} \frac{P^2}{P P^3} \frac{1}{\frac{1}{2} \left(\frac{3}{2}\right)^3} \frac{\left(\frac{1}{1 + \epsilon}\right)^2}{\frac{1}{1 + \epsilon} \frac{1}{(1 + \epsilon)^3}} = \frac{(1 - \epsilon)^2}{\epsilon^4} \frac{1}{P^2} \frac{(1 + \epsilon)^2}{27/16}$$

(Q2 cont.)

$p = \text{total pressure} = 2.00 \text{ bar}$

$$K = \frac{16}{27} \frac{(1-\epsilon)^2(1+\epsilon)^2}{\epsilon^4} \frac{1}{p^2} = 10.06$$

$$\sqrt{K} = \sqrt{\frac{16}{27} \frac{(1-\epsilon)^2(1+\epsilon)^2}{\epsilon^4} \frac{1}{p^2}} = \sqrt{\frac{16}{27}} \frac{(1-\epsilon)(1+\epsilon)}{\epsilon^2} \frac{1}{p}$$

$$p \sqrt{\frac{27}{16}} \sqrt{K} = \frac{(1-\epsilon)(1+\epsilon)}{\epsilon^2} = \frac{1-\epsilon^2}{\epsilon^2}$$

$$\left(p \sqrt{\frac{27}{16}} \sqrt{K} \right) \epsilon^2 = 1 - \epsilon^2$$

$$\left[1 + p \sqrt{\frac{27}{16}} \sqrt{K} \right] \epsilon^2 = 1 \quad \epsilon^2 = \frac{1}{1 + p \sqrt{\frac{27}{16}} \sqrt{K}}$$

$$\epsilon = \sqrt{\frac{1}{1 + p \sqrt{\frac{27}{16}} \sqrt{K}}} = \sqrt{\frac{1}{1 + 2.00 \sqrt{\frac{27(10.06)}{16}}}} = 0.329$$

ammonia is 32.9% dissociated at 500K and 2.00 bar

Check!



$$p = 2.00 \text{ bar}$$

$$\epsilon = 0.329$$

$$K = 10.06$$

$$P_{N_2} = \frac{\epsilon/2}{1+\epsilon} p = 0.247 \text{ bar}$$

$$P_{H_2} = \frac{3\epsilon/2}{1+\epsilon} p = 0.743 \text{ bar}$$

$$P_{NH_3} = \frac{1-\epsilon}{1+\epsilon} p = 1.010 \text{ bar}$$

$$\frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(1.010)^2}{0.247 (0.743)^3} = 10.07 \quad \checkmark$$

yes!

heterogeneous (multi-phase) chemical equilibrium



3 phases: solid CaCO_3 , solid CaO , CO_2 gas

equilibrium constant $K = P_{\text{CO}_2}/P^\circ$ ($P^\circ = 1 \text{ bar}$)

$K = P_{\text{CO}_2}$

a) equilibrium constant K ?

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

$$= \Delta G_f^\circ(\text{CaO}, s) + \Delta G_f^\circ(\text{CO}_2, g) - \Delta G_f^\circ(\text{CaCO}_3, s)$$

$$= (-604.03) + (-394.359) - (-1128.79) \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G^\circ = 130.401 \text{ kJ mol}^{-1} \quad \ln K = -\Delta G^\circ/RT$$

$$K = e^{-\Delta G^\circ/RT} = e^{-(130401)/(8.314 \cdot 298.15)} = e^{-52.60}$$

$K = 6.423 \times 10^{-23}$

b) ΔH° for the reaction $\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g)$?

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

$$= \Delta H_f^\circ(\text{CaO}, s) + \Delta H_f^\circ(\text{CO}_2, g) - \Delta H_f^\circ(\text{CaCO}_3, s)$$

$$= -635.09 + (-393.509) - (-1206.92) \text{ kJ mol}^{-1}$$

$\Delta H^\circ = 178.321 \text{ kJ mol}^{-1}$

(Q3 cont.)

c) at 25 °C $K = 1.423 \times 10^{-23} = P_{CO_2}$

at what temperature is $K = 1.00 \text{ bar } CO_2$?

assuming the standard enthalpy change of the reaction is constant:

$$\frac{d \ln K}{d \frac{1}{T}} = -\frac{\Delta H^\circ}{R} = \text{constant} = \frac{\Delta \ln K}{\Delta \frac{1}{T}} = \frac{\ln K_2 - \ln K_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$T_1 = 298.15 \text{ K (25 °C)}$$

$$T_2 = ?$$

$$K_1 = 1.423 \times 10^{-23}$$

$$K_2 = 1.00$$

Solve: $-\frac{\Delta H^\circ}{R} = \frac{\ln K_2 - \ln K_1}{\frac{1}{T_2} - \frac{1}{T_1}}$

$$\frac{1}{T_2} - \frac{1}{T_1} = -\frac{R}{\Delta H^\circ} (\ln K_2 - \ln K_1) = -\frac{8.314}{178321} [\ln(1.423 \times 10^{-23}) - \ln(1.00)]$$

$$\frac{1}{T_2} - \frac{1}{T_1} = 0.002453$$

$$\frac{1}{T_2} = \frac{1}{298.15} - 0.002453$$

$$\frac{1}{T_2} = 0.0009010 \text{ K}^{-1}$$

$$T_2 = 1110 \text{ K}$$

$$(837^\circ\text{C})$$

d) heating $CaCO_3(s)$ [from limestone deposits]

is used to make CaO , the active ingredient of cement used to make concrete. CaO is also an important industrial base, second only to $NaOH$.