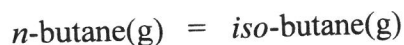


*Your lowest assignment mark will not be used to calculate your average assignment mark. So if you've handed in all the mandatory assignments (#1,2,3,5,6,7), and are happy with the results, a zero mark for #9 will not affect your course mark.

1. This question refers to the reaction



$$\begin{aligned} \text{data at } 25\text{ }^\circ\text{C} \\ \Delta G_{\text{fm}}^\circ(iso\text{-butane, g}) &= -20.76\text{ kJ mol}^{-1} \\ \Delta G_{\text{fm}}^\circ(n\text{-butane, g}) &= -17.03\text{ kJ mol}^{-1} \end{aligned}$$

- [3] At 25 °C, show:

- the standard Gibbs energy change $\Delta G_{\text{R}}^\circ$ for the reaction is -3730 J mol^{-1}
- the equilibrium constant for the reaction is $K = 4.50$
- 1.00 mol of pure *n*-butane reacts to form an equilibrium mixture containing 0.182 mol *n*-butane and 0.818 mol *iso*-butane.

2. *But wait!* $\Delta G_{\text{R}}^\circ$ for the conversion of *n*-butane to *iso*-butane is negative, indicating a spontaneous reaction. Why isn't *n*-butane completely converted to *iso*-butane? To answer this important question for chemical reaction equilibrium, show:

- the Gibbs energy change for converting 1.00 mole pure *n*-butane to $1.00 - \epsilon$ mole pure *n*-butane and ϵ mol pure *iso*-butane is $\epsilon \Delta G_{\text{R}}^\circ$
- the Gibbs energy change for mixing $1.00 - \epsilon$ mole pure *n*-butane and ϵ mole pure *iso*-butane is $RT[\epsilon \ln \epsilon + (1 - \epsilon) \ln(1 - \epsilon)]$.

- [5] c) From a and b, the Gibbs energy change for converting 1.00 mole pure *n*-butane to a mixture of $1.00 - \epsilon$ mole *n*-butane and ϵ mole *iso*-butane is

$$\Delta G = \epsilon \Delta G_{\text{R}}^\circ + RT[\epsilon \ln \epsilon + (1 - \epsilon) \ln(1 - \epsilon)]$$

- Use $d\Delta G / d\epsilon = 0$ locate the minimum in ΔG .
- Show the equilibrium value of ϵ is 0.818 mol.
- Explain why $\Delta G_{\text{R}}^\circ$ for the reaction $n\text{-butane(g)} = iso\text{-butane(g)}$ is negative, but *n*-butane is only partially (81.8 %) converted to *iso*-butane.

3. Standard Gibbs energies of formation and standard enthalpies of formation can be used to investigate phase equilibrium. To illustrate this point, calculate

- the standard Gibbs energy change for $\text{Hg(l)} = \text{Hg(g)}$
- the vapor pressure of liquid mercury at 25 °C
- the vapor pressure of liquid mercury at 100 °C.

$$\begin{aligned} \text{data at } 25\text{ }^\circ\text{C} \\ \Delta G_{\text{fm}}^\circ(\text{Hg, g}) &= 31.820\text{ kJ mol}^{-1} \\ \Delta H_{\text{fm}}^\circ(\text{Hg, g}) &= 61.317\text{ kJ mol}^{-1} \end{aligned}$$

4. a) Give two reasons why $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$ is not a universal equation of state.

[4] b) Explain why $p_r = \frac{8}{3} \frac{T_r}{V_r - \frac{1}{3}} - \frac{3}{V_r^2}$ is a universal equation of state.

c) Use the equation given in part b to show the reduced compressibility defined by

$$\kappa_r = -\frac{1}{V_r} \left(\frac{\partial V_r}{\partial p_r} \right)_{T_r}$$

is infinite at the critical point.

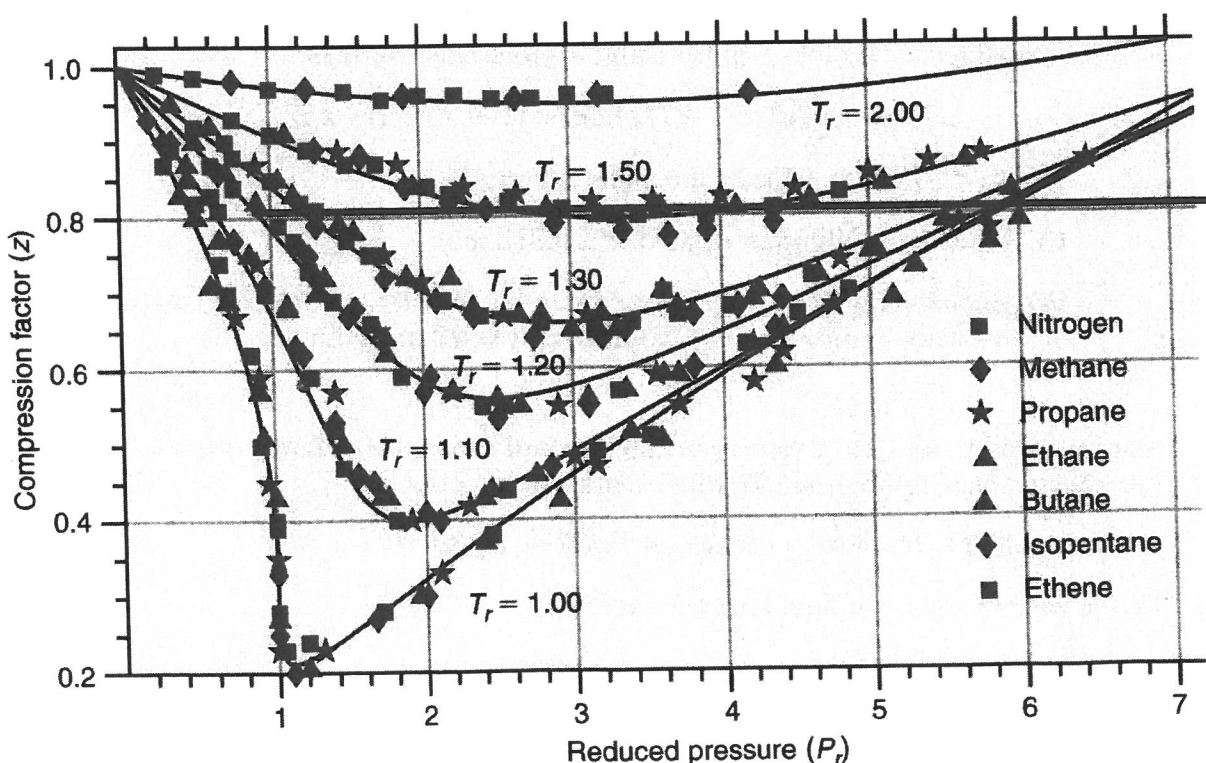
5. A 5.00 L tank is filled with xenon gas (MW 131.3 g mol⁻¹) at 320 K and 70.0 bar.

a) Xenon is a rare and valuable gas, costing about 5 USD per gram. Calculate the dollar value of the xenon in the tank using the ideal gas law.

b) The critical temperature and critical pressure of xenon are 290 K and 58.4 bar, respectively. Suggest why the answer to a might be unreliable.

[4]

c) Use the law of corresponding states and the graph below to calculate an accurate dollar value for the xenon in the tank.



(Q1)



$$\begin{aligned} \text{a) } \Delta G_R^\circ &= \Delta G_{fm}^\circ (\text{iso-butane}) - \Delta G_{fm}^\circ (\text{n-butane}) \\ &= -20.76 - (-17.03) \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta G_R^\circ = -3.73 \text{ kJ mol}^{-1} = -3730 \text{ J mol}^{-1}$$

b) equilibrium constant K

$$\begin{aligned} K &= \exp\left(-\frac{\Delta G_R^\circ}{RT}\right) \left(= \frac{P_{\text{iso}}}{P_n} = \frac{\frac{n_{\text{iso}}RT}{V}}{\frac{n_n RT}{V}} = \frac{n_{\text{iso}}}{n_n} \right) \\ &= \exp\left(-\frac{-3730 \text{ J}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right) \end{aligned}$$

$$K = \exp(1.505) = 4.503$$

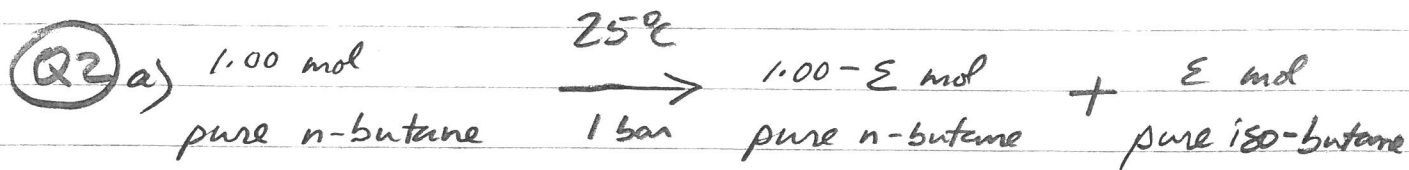
c) $n\text{-butane} = \text{iso-butane}$

initially: 1.00 mol 0

equilibrium: 1.00 - x mol x mol

$$K = \left(\frac{n_{\text{iso}}}{n_n}\right)_{\text{equil.}} = \frac{x}{1.00 - x} = 4.50$$

$$x = (4.50 / 5.50) \text{ mol} = 0.818 \text{ mol iso-butane}$$



$$\Delta G_R^\circ = (1.00 - \epsilon) \Delta G_{fm}^\circ(\text{n-but}) + \epsilon \Delta G_{fm}^\circ(\text{iso-but}) - (1.00 \text{ mol}) \Delta G_{fm}^\circ(\text{n-but})$$

$$= \epsilon [\Delta G_{fm}^\circ(\text{iso-but}) - \Delta G_{fm}^\circ(\text{n-but})]$$

$$\boxed{\Delta G_R^\circ = \epsilon \Delta G_{fm}^\circ} \quad (\text{REACTION ONLY})$$

at 25°C and 1 bar :

b) mix $1.00 - \epsilon \text{ mol}$ pure n-butane and $\epsilon \text{ mol}$ pure iso-butane

$$\Delta G_{\text{mix}} = n_n RT \ln x_n + n_{\text{iso}} RT \ln x_{\text{iso}}$$

$$= (1 - \epsilon) RT \ln \left(\frac{1 - \epsilon}{1 - \epsilon + \epsilon} \right) + \epsilon RT \ln \left(\frac{\epsilon}{1 - \epsilon + \epsilon} \right)$$

$$\boxed{\Delta G_{\text{mix}} = RT [(1 - \epsilon) \ln(1 - \epsilon) + \epsilon \ln \epsilon]} \quad (\text{MIXING ONLY})$$

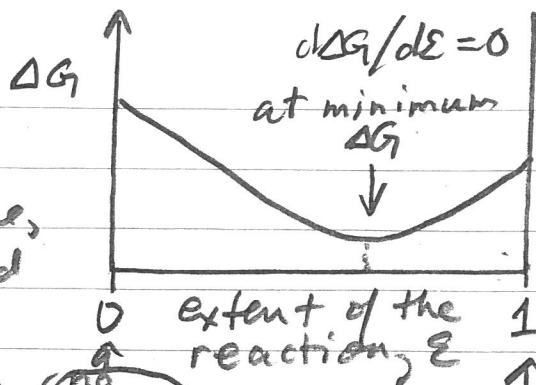
c) 1.00 mol pure n-butane \rightarrow mixture of $(1 - \epsilon) \text{ n-butane} + \epsilon \text{ iso-butane}$

$$\Delta G = \Delta G_{\text{reaction}} (\text{REACTION ONLY}) + \Delta G_{\text{mix}} (\text{MIXING ONLY})$$

$$\boxed{\Delta G = \epsilon \Delta G_R^\circ + RT [\epsilon \ln \epsilon + (1 - \epsilon) \ln(1 - \epsilon)]}$$

(Q2 c) cont.)

i) Starting with 1.00 mol pure n-butane, equilibrium is reached when ΔG reaches the minimum possible value



at minimum

$$\frac{d\Delta G}{d\varepsilon} = 0$$

$$0 = \frac{d}{d\varepsilon} \left\{ \varepsilon \Delta G_R^\circ + RT \left[\varepsilon \ln \varepsilon + (1-\varepsilon) \ln(1-\varepsilon) \right] \right\}$$

$$0 = \Delta G_R^\circ + RT \left[\frac{\varepsilon}{\varepsilon} + (\ln \varepsilon)(1) + (1-\varepsilon) \left(\frac{1}{1-\varepsilon} \right) + (\ln(1-\varepsilon))(-1) \right]$$

$$0 = \Delta G_R^\circ + \left[\ln \varepsilon - \ln(1-\varepsilon) \right] RT = \Delta G_R^\circ + RT \ln \left(\frac{\varepsilon}{1-\varepsilon} \right) = 0$$

(minimum ΔG)

ii) $\ln \left(\frac{\varepsilon}{1-\varepsilon} \right) = -\frac{\Delta G_R^\circ}{RT} = 1.505$ (from Q1 b)

$$\frac{\varepsilon}{1-\varepsilon} = e^{1.505} = 4.50 \Rightarrow \varepsilon = 0.818$$

(from Q1 c)

iii) ΔG_R° is negative for the conversion of pure n-butane to pure iso-butane. But the reaction does not go to completion, why? The actual conversion of n-butane to iso-butane is only 81.8% complete because the Gibbs energy of mixing n-butane and iso-butane gives a lower Gibbs energy than 100% reaction. (see sketch above)

Q3 a) liquid mercury \rightleftharpoons mercury vapor



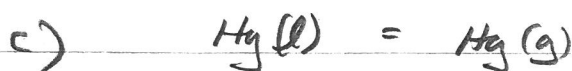
$$\begin{aligned}\Delta G_R^\circ &= \Delta G_{fm}^\circ(\text{Hg}, g) - \Delta G_{fm}^\circ(\text{Hg}, l) \\ &= \Delta G_{fm}^\circ(\text{Hg}, g) = \boxed{31.820 \text{ kJ mol}^{-1}} \quad (\text{at } 25^\circ\text{C})\end{aligned}$$

① pure element in its most stable standard state



equilibrium constant $K = P_{\text{Hg}} = e^{-\Delta G_R^\circ/RT}$

$$\begin{aligned}P_{\text{Hg}} &= \exp\left[-\frac{31,820 \text{ J}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right] \\ &= \exp(-12.84) = \boxed{2.661 \times 10^{-6} \text{ bar}}\end{aligned}$$



ΔH_R° assumed to be constant, no other information given

$$\Delta H_R^\circ = \Delta H_{fm}^\circ(\text{Hg}, g) - \Delta H_{fm}^\circ(\text{Hg}, l) = 61.317 \text{ kJ mol}^{-1} - 0$$

van't Hoff equation $\frac{d \ln K}{d \frac{1}{T}} = -\frac{\Delta H_R^\circ}{R} \Rightarrow d \ln K = -\frac{\Delta H_R^\circ}{R} d \frac{1}{T}$

$$\int d \ln K = -\frac{\Delta H_R^\circ}{R} \int d \frac{1}{T} \Rightarrow \ln K_{373.15\text{K}} - \ln K_{298.15\text{K}} = -\frac{\Delta H_R^\circ}{R} \left(\frac{1}{373.15\text{K}} - \frac{1}{298.15\text{K}} \right)$$

$$\ln K_{373.15\text{K}} = -12.84 - \frac{61317 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{373.15\text{K}} - \frac{1}{298.15\text{K}} \right)$$

(Q3 c) cont.)

$$\begin{aligned}\ln K_{373.15\text{ K}} &= \ln P_{\text{Hg}}^{373.15\text{ K}} \\ &= -12.84 + 4.972 = -7.87\end{aligned}$$

$$P_{\text{Hg}} \text{ at } 373.15\text{ K} \text{ (100 }^\circ\text{C)} = e^{-7.87} \text{ bar}$$

$$P_{\text{Hg}} = 0.000383 \text{ bar at } 100^\circ\text{C}$$

(144 times larger P_{Hg} pressure than at 25°C)

(Q4) a)
$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

not a universal equation of state because:

* P, T, V_m are in "human-defined" units (e.g. bar, K, $\frac{\text{L}}{\text{mol}}$)

* a, b parameters are specific to each gas (not universal)

* molar gas constant R is in "human-defined" units

b)
$$P_r = \frac{8}{3} \frac{TR}{V_r - \frac{1}{3}} - \frac{3}{V_r^2} \Rightarrow \text{"universal" equation of state}$$

no "human-defined" units or gas-specific parameters

(Q4 cont.)

c) "reduced" compressibility

$$\kappa_r = -\frac{1}{V_r} \left(\frac{\partial V_r}{\partial P_r} \right)_{T_r} \quad \text{in terms of reduced pressures (P_r) and reduced volumes (V_r)}$$

given:

$$P_r = \frac{8}{3} \frac{T_r}{V_r - \frac{1}{3}} - \frac{3}{V_r^2} \Rightarrow \left(\frac{\partial V_r}{\partial P_r} \right)_{T_r} \text{ is not easily evaluated}$$

but
(inverse rule)

$$\left(\frac{\partial V_r}{\partial P_r} \right)_{T_r} = \frac{1}{\left(\frac{\partial P_r}{\partial V_r} \right)_{T_r}} \quad \text{is easily evaluated}$$

$$\begin{aligned} \left(\frac{\partial P_r}{\partial V_r} \right)_{T_r} &= \left[\frac{\partial}{\partial V_r} \left(\frac{8}{3} \frac{T_r}{V_r - \frac{1}{3}} - \frac{3}{V_r^2} \right) \right]_{T_r} \\ &= \frac{8}{3} T_r \left(\frac{-1}{\left(V_r - \frac{1}{3} \right)^2} \right) - 3(-2) V_r^{-3} \end{aligned}$$

at the critical point ($T_r = 1$, $V_r = 1$)

$$\begin{aligned} \left(\frac{\partial P_r}{\partial V_r} \right)_{T_r} &= -\frac{8}{3} (1) \frac{1}{\left(1 - \frac{1}{3} \right)^2} + 6(1)^{-3} \\ &= -\frac{8}{3} \frac{1}{\left(\frac{2}{3} \right)^2} + 6 = -6 + 6 = 0 \end{aligned}$$

(Q4 c) cont.)

This means $\kappa_T = -\frac{1}{V_r} \left(\frac{\partial V_r}{\partial P_r} \right)_{T_r}$

$$= -\frac{1}{V_r} \frac{1}{\left(\frac{\partial P_r}{\partial V_r} \right)_{T_r}}$$

$$= \left(\frac{-1}{1} \right) \left(\frac{1}{0} \right) \quad \text{at } V_r = 1 \text{ (critical point)}$$

$$= \infty \quad \text{yikes! infinitely compressible!}$$

Q5

Xe gas at 320K and 70.0 bar
in a 5.00 L tank

a) using the ideal gas law, the number of moles of Xe in the tank is

$$n = \frac{PV}{RT} = \frac{(70.0 \text{ bar})(5.00 \text{ L})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(320 \text{ K})}$$

$$n = 13.15 \text{ mol}$$

$$\text{value} = (13.15 \text{ mol}) \left(\frac{131.3 \text{ g}}{\text{mol}} \right) \left(\frac{5 \text{ USD}}{\text{g}} \right)$$

$$= \boxed{8,630 \text{ USD}}$$

(Q5 cont.)

b) The xenon gas in the tank is at 320 K and 70.0 bar.

This temperature and this pressure are close to the critical temperature (290 K) and critical pressure (58.4 bar) of xenon, where xenon gas is strongly nonideal ($Z \approx \frac{1}{3}$) and close to liquefaction.

The ideal gas law $PV = nRT$ is not expected to be reliable under these conditions.
($Z_{\text{ideal}} = 1$)

c) xenon at 320 K and 70.0 bar

$$\left. \begin{aligned} T_r &= \frac{T}{T_c} = \frac{320 \text{ K}}{290 \text{ K}} = 1.10 \\ P_r &= \frac{P}{P_c} = \frac{70.0 \text{ bar}}{58.4 \text{ bar}} = 1.20 \end{aligned} \right\} \begin{array}{l} \text{read} \\ Z = 0.58 \\ \text{from the} \\ \text{graph} \end{array}$$

$$\boxed{Z = 0.58} = \frac{PV}{nRT} \quad n = \frac{PV}{RT} \frac{1}{Z}$$

$$n = (n_{\text{ideal}}) \frac{1}{Z} = n_{\text{ideal}} \frac{1}{0.58} \quad (72\% \text{ more cash!})$$

$$\text{value} = (8630 \text{ USD}) \frac{1}{0.58} = \boxed{14,900 \text{ USD}}$$