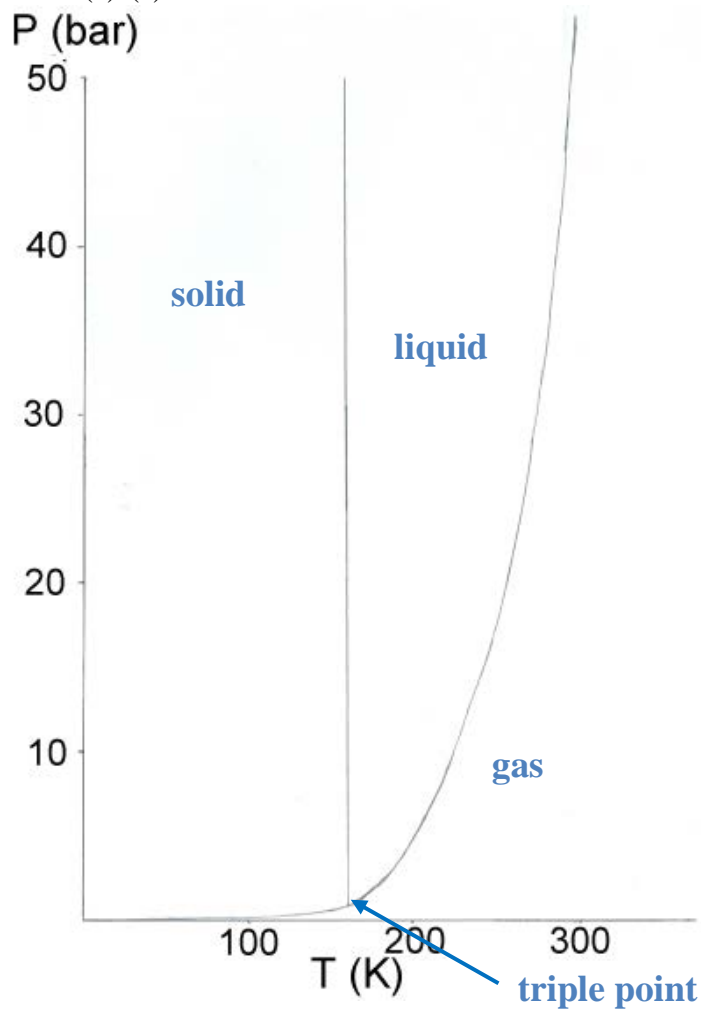


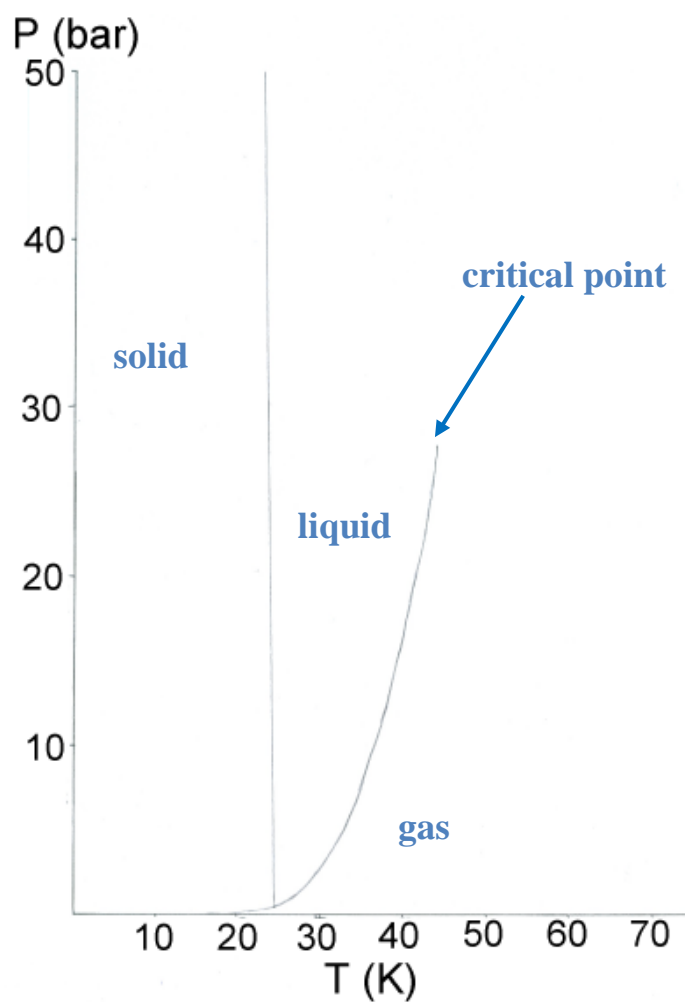
Answers to Practice Test Questions 8 Effect of Temperature on Equilibrium

1.

(a)-(c)



xenon



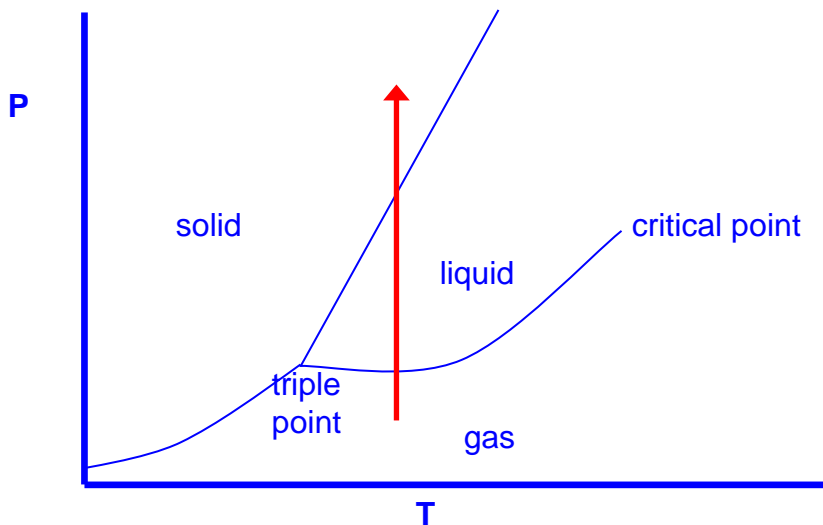
neon

- (d) The normal boiling point of the noble gas on the left is higher so it must be the larger noble gas (xenon).

Find normal boiling point by finding the temperature along the liquid/gas curve at $P = 1$ bar. The gas on the left (xenon) has a normal boiling point of 165K; the gas on the right (neon) has a normal boiling point of 27K.

Note that you cannot compare critical points or triple points because you must compare points at either the same pressure (e.g. normal boiling points are always at 1 atm \approx 1 bar) or same temperature to be able to draw any conclusions about behaviour.

2.



Assume a normal phase diagram (as shown above).

The substance will begin as a gas. As it is compressed, its density increases until it becomes a liquid. Continued compression increases the density further until the substance becomes a solid. This progression is shown by the red arrow on the phase diagram.

3. While this question can be solved 'from scratch' using activities and equilibrium constant expressions, it's easier to just use Raoult's law (which is derived from those activities and equilibrium constant expressions): $p_{H_2O} = X_{H_2O} \cdot p^\circ_{H_2O}$

Either way, you will need to calculate the mole fraction of water.

Step 1: Calculate the moles of each species in solution

$$n_{H_2O} = 300 \text{ g} \times \frac{1 \text{ mol}}{18.0152 \text{ g}} = 16.6526 \text{ mol} = 16.7 \text{ mol } H_2O$$

To calculate the moles of each ion in solution, it is easiest to calculate the moles of $(NH_4)_2SO_4$ then use mole ratios to calculate the moles of NH_4^+ and SO_4^{2-} .

$$n_{(NH_4)_2SO_4} = 50 \text{ g} \times \frac{1 \text{ mol}}{132.140 \text{ g}} = 0.38 \text{ mol } (NH_4)_2SO_4$$

$$n_{NH_4^+} = 0.38 \text{ mol } (NH_4)_2SO_4 \times \frac{2 \text{ mol } NH_4^+}{1 \text{ mol } (NH_4)_2SO_4} = 0.76 \text{ mol } NH_4^+$$

$$n_{SO_4^{2-}} = 0.38 \text{ mol } (NH_4)_2SO_4 \times \frac{1 \text{ mol } SO_4^{2-}}{1 \text{ mol } (NH_4)_2SO_4} = 0.38 \text{ mol } SO_4^{2-}$$

Step 2: Calculate the mole fraction of water in the solution

$$X_{H_2O} = \frac{n_{H_2O}}{(n_{H_2O}) + (n_{NH_4^+}) + (n_{SO_4^{2-}})} = \frac{16.7 \text{ mol}}{(16.7 \text{ mol}) + (0.76 \text{ mol}) + (0.38 \text{ mol})} = 0.936$$

Step 3: Calculate the vapour pressure above the solution

$$p_{H_2O} = X_{H_2O} \cdot p^\circ_{H_2O} = (0.936)(7373 \text{ Pa}) = 6902 \text{ Pa} = 6.90 \times 10^3 \text{ Pa} = 6.90 \text{ kPa}$$

Step 4: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

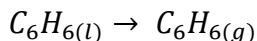
The dissolved salt lowers the vapour pressure of water above the solution.

4. The boiling point of benzene at 0.025 bar is the temperature at which the equilibrium vapour pressure of benzene is 0.025 bar (since boiling point is the temperature at which vapour pressure = atmospheric pressure and, here, the “atmosphere” has a pressure of 0.025).

You have been given the normal boiling point of benzene (i.e. the temperature at which the equilibrium vapour pressure of benzene is 1 atm. So, that makes this a “two temperatures; two equilibrium constants” question – which requires the use of $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

The key to these types of questions is to be organized! Make sure that K_1 is the equilibrium constant corresponding to T_1 (and that K_2 corresponds to T_2)!

Step 1: Write a balanced chemical equation for the reaction (phase change)



Step 2: Work out how to calculate activities for all reactants and products

$$a_{C_6H_{6(l)}} = 1 \qquad a_{C_6H_{6(g)}} = \frac{p_{C_6H_{6(g)}}}{1 \text{ bar}}$$

Step 3: Write equilibrium constant expression for the reaction (phase change) and simplify where possible.

$$K = \frac{a_{C_6H_{6(g)}}}{a_{C_6H_{6(l)}}} = \frac{\left(\frac{p_{C_6H_{6(g)}}}{1 \text{ bar}}\right)}{(1)} = \frac{p_{C_6H_{6(g)}}}{1 \text{ bar}}$$

Step 4: Calculate equilibrium constants, and match them to the corresponding temperature

$$T_1 = 80.10 \text{ }^\circ\text{C} = 353.25 \text{ K} \qquad \text{normal boiling point } (p_{C_6H_{6(g)}} = 1 \text{ atm})$$

$$K_1 = \frac{p_{C_6H_{6(g)}}}{1 \text{ bar}} = \frac{1 \text{ atm}}{1 \text{ bar}} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} = 1.01325$$

$$T_2 = ??? \qquad \text{boiling point at 0.025 bar } (p_{C_6H_{6(g)}} = 0.025 \text{ bar})$$

$$K_2 = \frac{p_{C_6H_{6(g)}}}{1 \text{ bar}} = \frac{0.025 \text{ bar}}{1 \text{ bar}} = 0.025$$

Step 5: Look up (or calculate) standard enthalpy change for the reaction (phase change)

$$\Delta_r H^\circ = +30.7 \frac{\text{kJ}}{\text{mol}} = 3.07 \times 10^4 \frac{\text{J}}{\text{mol}} \qquad \text{provided in question}$$

Step 6: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{0.025}{1.01325}\right) = \left(\frac{3.07 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}}}\right)\left(\frac{1}{353.25 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{\ln\left(\frac{0.025}{1.01325}\right)(8.314 \ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}})}{3.07 \times 10^4 \frac{\text{J}}{\text{mol}}} = \left(\frac{1}{353.25 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{1}{T_2} = \frac{1}{353.25 \text{ K}} - \frac{\ln\left(\frac{0.025}{1.01325}\right)(8.314 \ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}})}{3.07 \times 10^4 \frac{\text{J}}{\text{mol}}}$$

$$\frac{1}{T_2} = \left(0.002 \ 830 \ 9 \frac{1}{\text{K}}\right) - \left(-0.001 \ 00 \frac{1}{\text{K}}\right)$$

$$\frac{1}{T_2} = 0.003 \ 83 \frac{1}{\text{K}}$$

$$T_2 = \frac{1}{0.003 \ 83 \frac{1}{\text{K}}} = 261 \text{ K} = -12 \text{ }^\circ\text{C}$$

Step 7: Check your work

Does your answer seem reasonable?

Since 0.025 bar is a much lower pressure than 1 atm, it makes sense that the boiling point at that (lower) pressure is much lower than the normal boiling point.

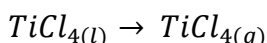
Step 8: Answer the question!

There was a verbal question attached to this calculation. It's easy to forget about that. Always re-read the question when you think you're done to make sure you answered everything!

Yes, benzene will boil at room temperature when the pressure is 0.025 bar. Its boiling point at this pressure is $-12\text{ }^\circ\text{C}$.

5. This is another "two temperatures; two equilibrium constants" question requiring the use of $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. In this case, we can use thermodynamic data to calculate the equilibrium constant at $25\text{ }^\circ\text{C}$ from the standard free energy change for the reaction.

Step 1: Write a balanced chemical equation for the reaction (phase change)



Step 2: Work out how to calculate activities for all reactants and products

$$a_{\text{TiCl}_{4(l)}} = 1 \qquad a_{\text{TiCl}_{4(g)}} = \frac{p_{\text{TiCl}_{4(g)}}}{1 \text{ bar}}$$

Step 3: Write equilibrium constant expression for the reaction (phase change) and simplify where possible.

$$K = \frac{a_{\text{TiCl}_{4(g)}}}{a_{\text{TiCl}_{4(l)}}} = \frac{\left(\frac{p_{\text{TiCl}_{4(g)}}}{1 \text{ bar}}\right)}{(1)} = \frac{p_{\text{TiCl}_{4(g)}}}{1 \text{ bar}}$$

Step 4: Calculate the standard free energy change for the reaction (phase change)

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = \Delta_f G^\circ(\text{TiCl}_{4(g)}) - \Delta_f G^\circ(\text{TiCl}_{4(l)})$$

$$\Delta_r G^\circ = \left(-726.7 \frac{\text{kJ}}{\text{mol}}\right) - \left(-737.2 \frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta_r G^\circ = 10.5 \frac{\text{kJ}}{\text{mol}}$$

Step 5: Calculate equilibrium constants, and match them to the corresponding temperature

$$T_1 = 25\text{ }^\circ\text{C} = 298.15 \text{ K}$$

standard conditions

$$\Delta_r G^\circ = -RT \ln K_1$$

$$\ln K_1 = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K_1 = -\frac{\left(10.5 \frac{\text{kJ}}{\text{mol}}\right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K_1 = -4.24$$

$$K_1 = e^{-4.24}$$

$$K_1 = 1.4 \times 10^{-2}$$

$$T_2 = ???$$

normal boiling point ($p_{\text{TiCl}_4(g)} = 1 \text{ atm}$)

$$K_2 = \frac{p_{\text{TiCl}_4(g)}}{1 \text{ bar}} = \frac{1 \text{ atm}}{1 \text{ bar}} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} = 1.01325$$

Step 6: Calculate the standard enthalpy change for the reaction (phase change)

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = \Delta_f H^\circ(\text{TiCl}_4(g)) - \Delta_f H^\circ(\text{TiCl}_4(l))$$

$$\Delta_r H^\circ = \left(-763.2 \frac{\text{kJ}}{\text{mol}}\right) - \left(-804.2 \frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta_r H^\circ = +41.0 \frac{\text{kJ}}{\text{mol}} = 4.10 \times 10^4 \frac{\text{J}}{\text{mol}}$$

Step 7: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{1.01325}{1.4 \times 10^{-2}}\right) = \left(\frac{4.10 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}\right) \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{\ln\left(\frac{1.01325}{1.4 \times 10^{-2}}\right) \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1}\right)}{4.10 \times 10^4 \frac{\text{J}}{\text{mol}}} = \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{1}{T_2} = \frac{1}{298.15 \text{ K}} - \frac{\ln\left(\frac{1.01325}{1.4 \times 10^{-2}}\right) \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1}\right)}{4.10 \times 10^4 \frac{\text{J}}{\text{mol}}}$$

$$\frac{1}{T_2} = \left(0.003354 \frac{1}{\text{K}}\right) - \left(0.000862 \frac{1}{\text{K}}\right)$$

$$\frac{1}{T_2} = 0.002492 \frac{1}{\text{K}}$$

$$T_2 = \frac{1}{0.002492 \frac{1}{\text{K}}} = 401.2 \text{ K} = 128.1 \text{ }^\circ\text{C}$$

Step 8: Check your work

Does your answer seem reasonable?

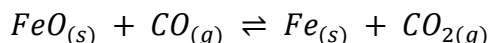
Since TiCl₄ is a liquid at room temperature, its normal boiling point should be higher than room temperature.

6. This is another “two temperatures; two equilibrium constants” question requiring the use of $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Again, keeping organized is key to success.

Because the equilibrium constant was provided directly (rather than indirectly in the form of pressure data), it is not necessary to calculate activities for this question.

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.



Step 2: Match equilibrium constants to the corresponding temperature

$$T_1 = 998 \text{ K}$$

$$T_2 = 298 \text{ K}$$

$$K_1 = 0.259$$

$$K_2 = ???$$

Step 3: Calculate the standard enthalpy change for the reaction

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = [\Delta_f H^\circ(\text{Fe}_{(s)}) + \Delta_f H^\circ(\text{CO}_{2(g)})] - [\Delta_f H^\circ(\text{FeO}_{(s)}) + \Delta_f H^\circ(\text{CO}_{(g)})]$$

$$\Delta_r H^\circ = \left[\left(0 \frac{\text{kJ}}{\text{mol}} \right) + \left(-393.5 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[\left(-272.0 \frac{\text{kJ}}{\text{mol}} \right) + \left(-110.5 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r H^\circ = -11.0 \frac{\text{kJ}}{\text{mol}} = -1.10 \times 10^4 \frac{\text{J}}{\text{mol}}$$

Step 4: Crunch the numbers

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left(\frac{K_2}{0.259} \right) = \left(\frac{-1.10 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \right) \left(\frac{1}{998 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\ln \left(\frac{K_2}{0.259} \right) = 3.11$$

$$\frac{K_2}{0.259} = e^{3.11}$$

$$\frac{K_2}{0.259} = 23$$

$$K_2 = (0.259)(23)$$

$$K_2 = 5.8$$

Step 5: Check your work

Does your answer seem reasonable?

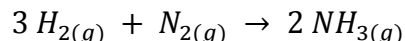
This reaction is exothermic ($\Delta_r H^\circ < 0$), so it is expected to have a larger equilibrium constant at the lower temperature.

7.

- (a) Equilibrium constants can be calculated from the standard free energy change for a reaction.

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.

**Step 2: Convert temperature to Kelvin (if necessary)**

$$T = 25^\circ \text{C} = 298.15 \text{ K}$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = \left(2 \Delta_f G^\circ(\text{NH}_{3(g)}) \right) - \left[3 \Delta_f G^\circ(\text{H}_{2(g)}) + \Delta_f G^\circ(\text{N}_{2(g)}) \right]$$

$$\Delta_r G^\circ = 2 \left(-16.4 \frac{\text{kJ}}{\text{mol}} \right) - \left[3 \left(0 \frac{\text{kJ}}{\text{mol}} \right) + \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r G^\circ = -32.8 \frac{\text{kJ}}{\text{mol}}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K = -\frac{\left(-32.8 \frac{\text{kJ}}{\text{mol}}\right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K = 13.2$$

$$K = e^{13.2}$$

$$K = 6 \times 10^5$$

Step 5: Check your work

Does your answer seem reasonable?

- (b) This is another “two temperatures; two equilibrium constants” question requiring the use of $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Again, keeping organized is key to success. Some of the steps were already taken care of in part (a).

Step 1: Match equilibrium constants to the corresponding temperature

$$T_1 = 298.15 \text{ K}$$

$$T_2 = 300 \text{ }^\circ\text{C} = 573.15 \text{ K}$$

$$K_1 = 6 \times 10^5$$

$$K_2 = ???$$

Step 2: Calculate the standard enthalpy change for the reaction

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = \left(2 \Delta_f H^\circ(\text{NH}_3(\text{g}))\right) - \left[3 \Delta_f H^\circ(\text{H}_2(\text{g})) + \Delta_f H^\circ(\text{N}_2(\text{g}))\right]$$

$$\Delta_r H^\circ = 2 \left(-45.9 \frac{\text{kJ}}{\text{mol}}\right) - \left[3 \left(0 \frac{\text{kJ}}{\text{mol}}\right) + \left(0 \frac{\text{kJ}}{\text{mol}}\right)\right]$$

$$\Delta_r H^\circ = -91.8 \frac{\text{kJ}}{\text{mol}} = -9.18 \times 10^4 \frac{\text{J}}{\text{mol}}$$

Step 3: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{6 \times 10^5}\right) = \left(\frac{-9.18 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}\right) \left(\frac{1}{298.15 \text{ K}} - \frac{1}{573.15 \text{ K}}\right)$$

$$\ln\left(\frac{K_2}{6 \times 10^5}\right) = -17.8$$

$$\frac{K_2}{6 \times 10^5} = e^{-17.8}$$

$$\frac{K_2}{6 \times 10^5} = 2 \times 10^{-8}$$

$$K_2 = (6 \times 10^5)(2 \times 10^{-8})$$

$$K_2 = 1 \times 10^{-2}$$

Step 4: Check your work

Does your answer seem reasonable?

This reaction is exothermic ($\Delta_r H^\circ < 0$), so it is expected to have a smaller equilibrium constant at the higher temperature.

- (c) The formula used to calculate K_2 was derived assuming that the enthalpy change and entropy change for a reaction are constant at all temperatures. This is a reasonable approximation but is not actually true. Since the value for $\Delta_r H$ varies somewhat with temperature, this formula can only be used to calculate approximate equilibrium constants.
- (d) The equilibrium constant for this reaction decreases as the temperature of reaction increases. This means that, at a lower temperature, more product can form before equilibrium is reached.
- (e) *Since you have already calculated K at 300 °C, you can determine whether or not the reaction is thermodynamically allowed at that temperature by calculating Q and comparing it to K .*

Step 1: Determine activities for all reactants and products

$$a_{N_2(g)} = \frac{50 \text{ bar}}{1 \text{ bar}} = 50 \qquad a_{NH_3(g)} = \frac{30 \text{ bar}}{1 \text{ bar}} = 30$$

$$a_{H_2(g)} = \frac{150 \text{ bar}}{1 \text{ bar}} = 150$$

Step 2: Calculate reaction quotient

$$Q = \frac{(a_{NH_3(g)})^2}{(a_{N_2(g)})(a_{H_2(g)})^3} = \frac{(30)^2}{(50)(150)^3} = 5.3 \times 10^{-6}$$

Step 3: Compare Q to K (at the appropriate temperature)

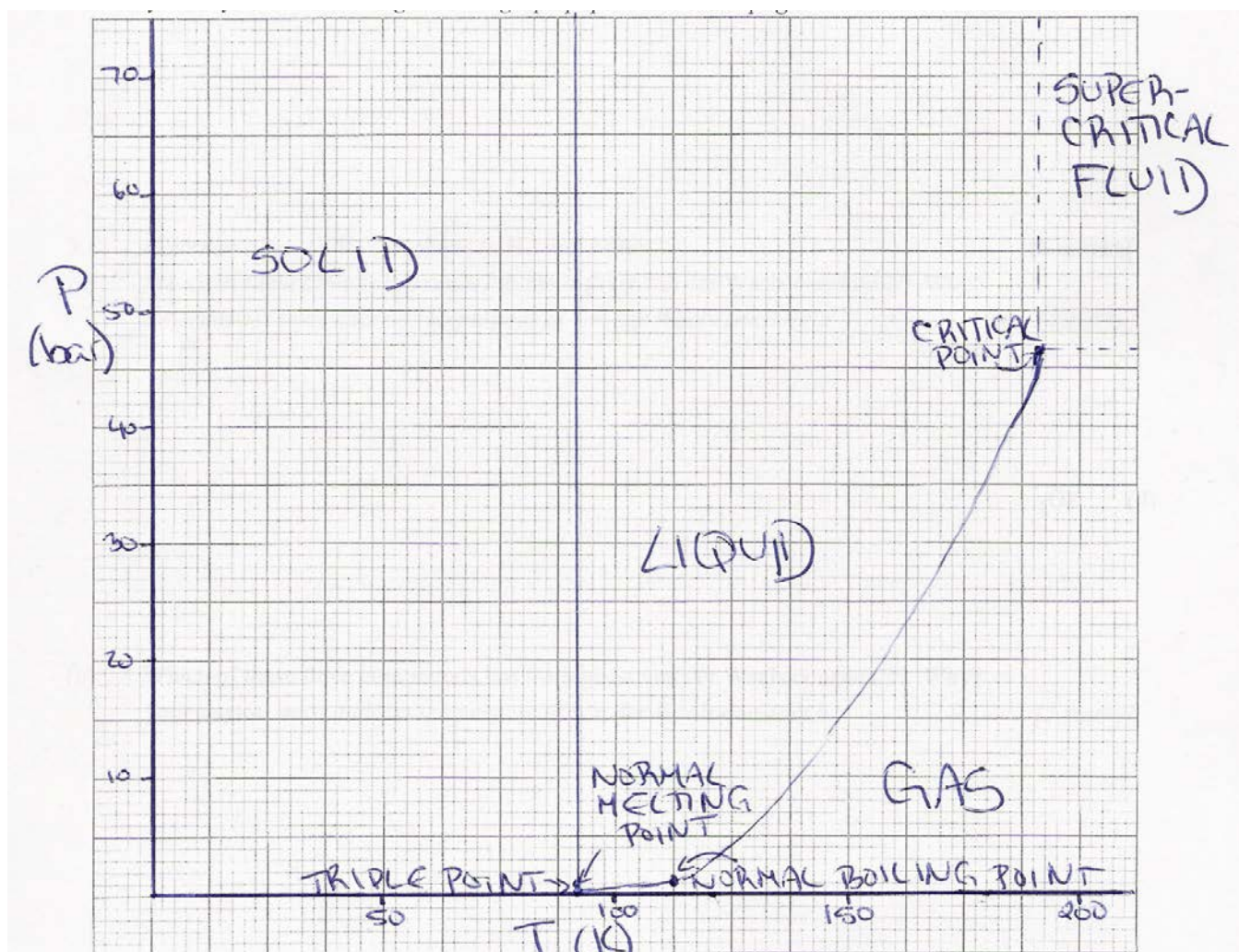
$$Q = 5.3 \times 10^{-6}$$

$$K = 1 \times 10^{-2}$$

$Q < K$ therefore the reaction is thermodynamically allowed under these conditions.

8.

(a)

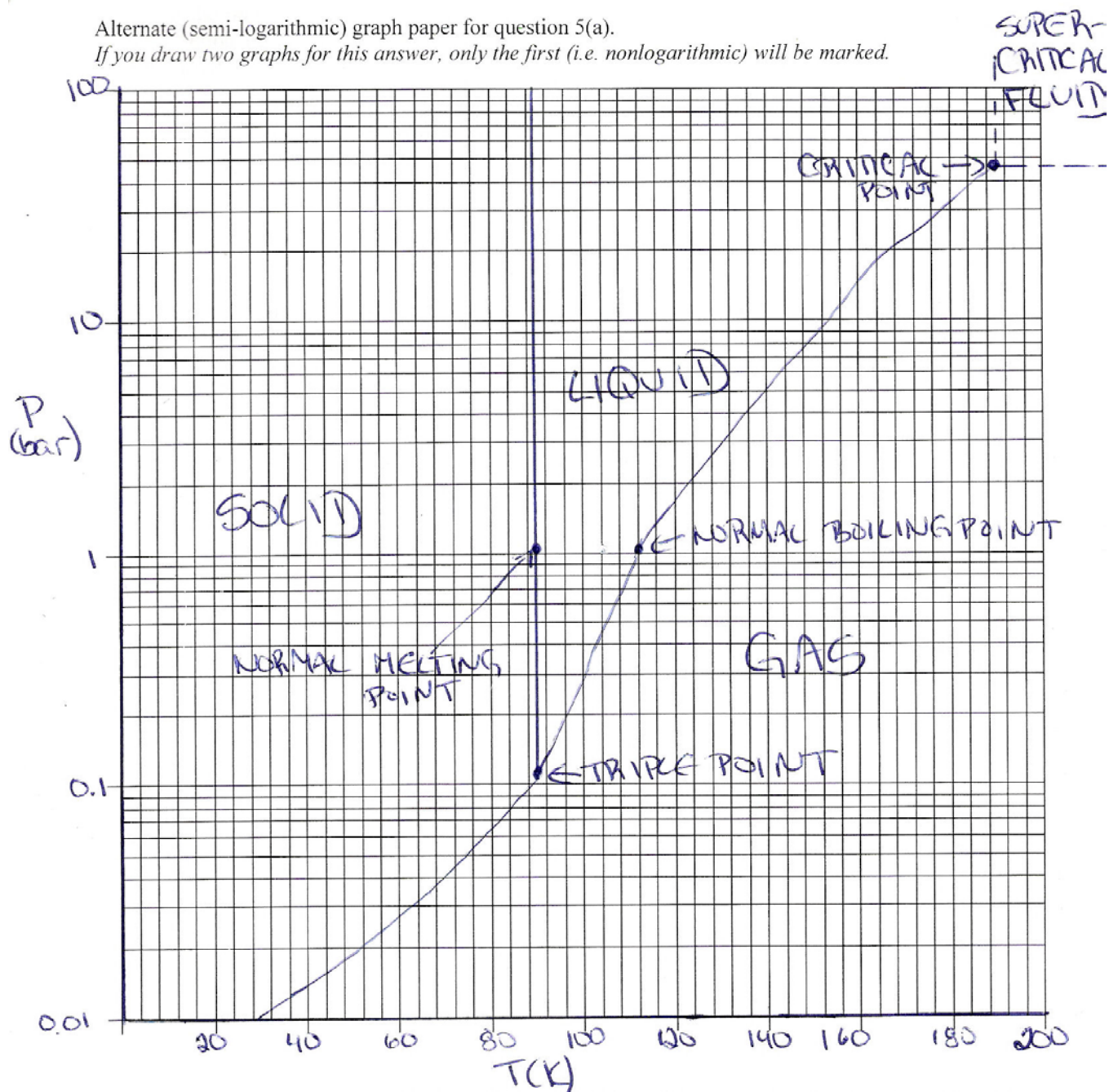


(b) sublimation

This pressure is BELOW the triple point, so liquid phase is not possible!

Alternate (semi-logarithmic) graph paper for question 5(a).

If you draw two graphs for this answer, only the first (i.e. nonlogarithmic) will be marked.



(b) sublimation

This pressure is BELOW the triple point, so liquid phase is not possible!

9.

(a) FALSE

Solutes increase the boiling point of solutions compared to the pure solvent. Since they decrease the vapor pressure of the solvent at any given temperature, it requires a higher temperature for the vapor pressure to be equal to the atmospheric pressure (which is when the liquid boils).

(b) FALSE

The free energy of the system decreases in a thermodynamically allowed process. The entropy of the universe increases in a thermodynamically allowed process, and $-\Delta_r G = -T\Delta S_{universe}$

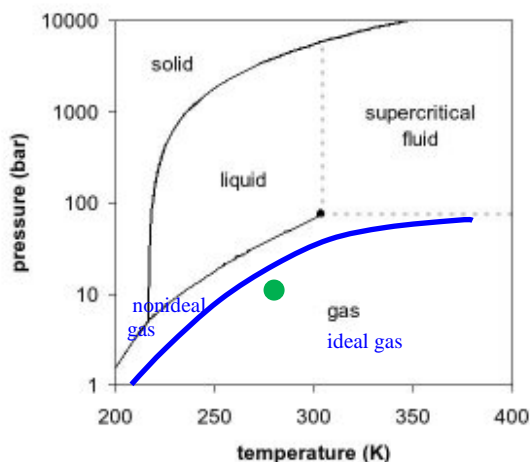
(c) FALSE

At equilibrium, $Q = K$.

Under standard conditions, $Q = 1$ (since all activities are 1 under standard conditions).

10.

(a)



Recall from CHEM 1000 that a gas behaves ideally when it has low density (therefore its particles take up negligible volume and experience negligible intermolecular forces). This occurs at relatively low pressure and or/high temperature. Nonideal behavior is observed at pressures almost (but not quite) high enough to compress the gas to a liquid.

(b) A supercritical fluid is a substance that is at a high enough pressure that it has the density of a liquid and a high enough temperature that its particles have the high average kinetic energy that would usually be associated with a gas.

(c)

i. *see the green dot on the diagram above*

ii. At 10 bar and 300 K, CO₂ is a gas. As the temperature is decreased, it condenses to a liquid then freezes to a solid.

iii. As the temperature decreases, the average kinetic energy of particles in the sample decreases. Having less kinetic energy to overcome intermolecular forces, the particles in the sample pack more densely so a liquid (then, at lower temperatures, a solid) forms.

11.

(a) Vapour pressure is the pressure exerted by molecules which have evaporated (or sublimed) out of a liquid (or solid) sample.

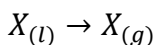
(b) Vapour pressure increases as temperature increases.

As temperature increases, the average kinetic energy of the particles in the sample increases.

Therefore, more particles within the sample will have enough energy to overcome intermolecular forces within the liquid (or solid) and escape into the gas phase.

As the number of particles in the gas phase increases, the pressure they exert increases.

(c) **Step 1: Write out the relevant balanced chemical equation (the reaction is liquid X evaporates to give gas X)**



Step 2: Write the equilibrium constant expression for this reaction

$$K = \frac{a_{X(g)}}{a_{X(l)}}$$

Step 3: Fill in the activities

$$a_{X(l)} = 1$$

$$a_{X(g)} = \frac{p_{X(g)}}{1 \text{ bar}}$$

$$K = \frac{a_{X(g)}}{a_{X(l)}} = \frac{\left(\frac{p_{X(g)}}{1 \text{ bar}}\right)}{1} = \frac{p_{X(g)}}{1 \text{ bar}}$$

Step 4: Substitute for K at each temperature and simplify to give the Clausius-Clapeyron equation. (p_1 is the vapour pressure at T_1 ; K_1 is the equilibrium constant at T_1)

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{\frac{p_2}{1 \text{ bar}}}{\frac{p_1}{1 \text{ bar}}}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

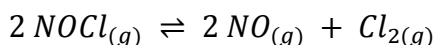
12.

(a)
$$K = \frac{(a_{NO(g)})^2 (a_{Cl_2(g)})}{(a_{NOCl(g)})^2}$$

(b) *Equilibrium constants can be calculated from the standard free energy change for a reaction. When this question was originally on a test, standard free energies of formation were not provided. With that limited set of data, it was best to calculate the standard enthalpy change for the reaction and the standard entropy change for the reaction then use those values to calculate the standard free energy change for the reaction. The standard enthalpy change for the reaction was necessary for part (c) anyway.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.



Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25\text{ }^{\circ}\text{C} = 298.15\text{ K}$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G^{\circ} = \sum \Delta_f G^{\circ}(\text{products}) - \sum \Delta_f G^{\circ}(\text{reactants})$$

$$\Delta_r G^{\circ} = [2 \Delta_f G^{\circ}(\text{NO}_{(g)}) + \Delta_f G^{\circ}(\text{Cl}_{2(g)})] - (2 \Delta_f G^{\circ}(\text{NOCl}_{(g)}))$$

$$\Delta_r G^{\circ} = \left[2 \left(86.55 \frac{\text{kJ}}{\text{mol}} \right) + \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] - 2 \left(66.08 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta_r G^{\circ} = 40.94 \frac{\text{kJ}}{\text{mol}}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G^{\circ} = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^{\circ}}{RT}$$

$$\ln K = -\frac{\left(40.94 \frac{\text{kJ}}{\text{mol}} \right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (298.15\text{ K})} \times \frac{1000\text{ J}}{1\text{ kJ}}$$

$$\ln K = -16.52$$

$$K = e^{-16.52}$$

$$K = 6.7 \times 10^{-8}$$

Step 5: Check your work

Does your answer seem reasonable? A positive standard free energy change should correspond to a small equilibrium constant (i.e. significantly smaller than 1).

- (c) This is another "two temperatures; two equilibrium constants" question requiring the use of $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Again, keeping organized is key to success.

Step 1: Match equilibrium constants to the corresponding temperature

$$T_1 = 298.15\text{ K}$$

$$T_2 = 745\text{ K}$$

$$K_1 = 6.7 \times 10^{-8}$$

$$K_2 = ???$$

Step 2: Calculate the standard enthalpy change for the reaction

$$\Delta_r H^{\circ} = \sum \Delta_f H^{\circ}(\text{products}) - \sum \Delta_f H^{\circ}(\text{reactants})$$

$$\Delta_r H^{\circ} = [2 \Delta_f H^{\circ}(\text{NO}_{(g)}) + \Delta_f H^{\circ}(\text{Cl}_{2(g)})] - (2 \Delta_f H^{\circ}(\text{NOCl}_{(g)}))$$

$$\Delta_r H^{\circ} = \left[2 \left(90.25 \frac{\text{kJ}}{\text{mol}} \right) + \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] - 2 \left(51.71 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta_r H^{\circ} = +77.08 \frac{\text{kJ}}{\text{mol}} = +7.708 \times 10^4 \frac{\text{J}}{\text{mol}}$$

Step 3: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{6.7 \times 10^{-8}}\right) = \left(\frac{7.708 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}\right) \left(\frac{1}{298.15\text{ K}} - \frac{1}{745\text{ K}}\right)$$

$$\ln\left(\frac{K_2}{6.7 \times 10^{-8}}\right) = 18.6$$

$$\frac{K_2}{6.7 \times 10^{-8}} = e^{18.6}$$

$$\frac{K_2}{6.7 \times 10^{-8}} = 1 \times 10^8$$

$$K_2 = (6.7 \times 10^{-8})(1 \times 10^8)$$

$$K_2 = 8$$

Step 4: Check your work

Does your answer seem reasonable?

This reaction is endothermic ($\Delta_r H^\circ > 0$), so it is expected to have a larger equilibrium constant at the higher temperature.

Alternatively, the question could be solved by calculating the free energy change at 745 K from the standard enthalpy change and standard entropy change (assuming that those two values do not vary significantly with temperature) using $\Delta G = \Delta H - T\Delta S$.

The free energy change at 745 K could then be used to calculate the equilibrium constant at that temperature using $\Delta G^\circ = -RT \ln K$. (This formula can be used at other temperatures – in which case, all activities must still be one.)

Please note that you CANNOT just use the standard free energy change calculated for 298.15 K in the above equation with $T = 745$. Free energy varies significantly with temperature! The temperature at which standard free energy is calculated must always match the temperature used in $\Delta G^\circ = -RT \ln K$ for the formula to be applicable.

This alternative approach also gives $K_2 = 8$.

- (d) *Since you have already calculated K at 745 K, you can determine whether or not the reaction is thermodynamically allowed at that temperature by calculating Q and comparing it to K .*

Step 1: Determine activities for all reactants and products

$$a_{\text{NOCl}_{(g)}} = \frac{0.05 \text{ bar}}{1 \text{ bar}} = 0.05$$

$$a_{\text{NO}_{(g)}} = \frac{0.41 \text{ bar}}{1 \text{ bar}} = 0.41$$

$$a_{\text{Cl}_{2(g)}} = \frac{0.32 \text{ bar}}{1 \text{ bar}} = 0.32$$

Step 2: Calculate reaction quotient

$$Q = \frac{(a_{\text{NO}_{(g)}})^2 (a_{\text{Cl}_{2(g)}})}{(a_{\text{NOCl}_{(g)}})^2} = \frac{(0.41)^2 (0.32)}{(0.05)^2} = 22 = 2 \times 10^1$$

Step 3: Compare Q to K (at the appropriate temperature)

$$Q = 2 \times 10^1$$

$$K = 8$$

$Q > K$ therefore the reaction is not thermodynamically allowed in the forward direction under these conditions. Instead, it will proceed in reverse (assuming that the kinetics allow for that).

13.

(a) 89.3 kPa

By definition, the vapour pressure at a boiling point is equal to the atmospheric pressure.

(b) *This question is most easily answered using Raoult's Law. Begin by calculating the mole fraction of water.*

Step 1: Calculate the moles of each species in solution

$$n_{H_2O} = 1000 \text{ g} \times \frac{1 \text{ mol}}{18.0152 \text{ g}} = 55.51 \text{ mol } H_2O$$

To calculate the moles of each ion in solution, it is easiest to calculate the moles of $MgCl_2$ then use mole ratios to calculate the moles of Mg^{2+} and Cl^- .

$$n_{Mg^{2+}} = 0.50 \text{ mol } MgCl_2 \times \frac{1 \text{ mol } Mg^{2+}}{1 \text{ mol } MgCl_2} = 0.50 \text{ mol } Mg^{2+}$$

$$n_{Cl^-} = 0.50 \text{ mol } MgCl_2 \times \frac{2 \text{ mol } Cl^-}{1 \text{ mol } MgCl_2} = 1.0 \text{ mol } Cl^-$$

Step 2: Calculate the mole fraction of water in the solution

$$X_{H_2O} = \frac{n_{H_2O}}{(n_{H_2O}) + (n_{Mg^{2+}}) + (n_{Cl^-})} = \frac{55.51 \text{ mol}}{(55.51 \text{ mol}) + (0.50 \text{ mol}) + (1.0 \text{ mol})} = 0.974$$

Step 3: Calculate the vapour pressure above the solution

$$p_{H_2O} = X_{H_2O} \cdot p^\circ_{H_2O} = (0.974)(89.3 \text{ kPa}) = 87.0 \text{ kPa}$$

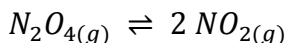
Step 4: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

The dissolved salt lowers the vapour pressure of water above the solution.

14. *Equilibrium constants can be calculated from the standard free energy change for a reaction.*

Step 1: Write a balanced chemical equation for the reaction



Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25 \text{ }^\circ\text{C} = 298.15 \text{ K}$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = [2 \Delta_f G^\circ(NO_{2(g)})] - [\Delta_f G^\circ(N_2O_{4(g)})]$$

$$\Delta_r G^\circ = 2 \left(51.31 \frac{\text{kJ}}{\text{mol}} \right) - \left(97.89 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta_r G^\circ = 4.73 \frac{\text{kJ}}{\text{mol}}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K = -\frac{\left(4.73 \frac{\text{kJ}}{\text{mol}} \right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K = -1.91$$

$$K = e^{-1.91}$$

$$K = 0.15$$

Step 5: Check your work

Does your answer seem reasonable? A positive standard free energy change should correspond to a small equilibrium constant (i.e. smaller than 1).

Now, the equilibrium constant at 25 °C can be used to calculate the temperature corresponding to a different equilibrium constant. That makes this another “two temperatures; two equilibrium constants” question requiring the use of $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

Start by calculating the equilibrium constant of interest (i.e. the one corresponding to the two pressures described in the question).

Step 6: Determine activities for all reactants and products

$$a_{N_2O_4(g)} = \frac{0.5 \text{ bar}}{1 \text{ bar}} = 0.5$$

$$a_{NO_2(g)} = \frac{0.5 \text{ bar}}{1 \text{ bar}} = 0.5$$

Step 7: Calculate the equilibrium constant for the pressures provided. This will be K_2 .
(The equilibrium constant at 25 °C is K_1 .)

$$K_2 = \frac{(a_{NO_2(g)})^2}{a_{N_2O_4(g)}}$$

$$K_2 = \frac{(0.5)^2}{(0.5)} = 0.5$$

Step 8: Match equilibrium constants to the corresponding temperature

$$T_1 = 298.15 \text{ K}$$

$$T_2 = ???$$

$$K_1 = 0.15$$

$$K_2 = 0.5$$

Step 9: Calculate the standard enthalpy change for the reaction

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = [2 \Delta_f H^\circ(NO_2(g))] - [\Delta_f H^\circ(N_2O_4(g))]$$

$$\Delta_r H^\circ = 2 \left(33.18 \frac{\text{kJ}}{\text{mol}}\right) - \left(9.16 \frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta_r H^\circ = +57.20 \frac{\text{kJ}}{\text{mol}} = +5.720 \times 10^4 \frac{\text{J}}{\text{mol}}$$

Step 10: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{0.5}{0.15}\right) = \left(\frac{5.720 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}}}\right) \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{\ln\left(\frac{0.5}{0.15}\right)(8.314 \ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}})}{5.720 \times 10^4 \frac{\text{J}}{\text{mol}}} = \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{1}{T_2} = \frac{1}{298.15 \text{ K}} - \frac{\ln\left(\frac{0.5}{0.15}\right)(8.314 \ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}})}{5.720 \times 10^4 \frac{\text{J}}{\text{mol}}}$$

$$\frac{1}{T_2} = \left(0.003 \ 354 \ 0 \frac{1}{\text{K}}\right) - \left(0.000 \ 18 \frac{1}{\text{K}}\right)$$

$$\frac{1}{T_2} = 0.003 \ 18 \frac{1}{\text{K}}$$

$$T_2 = \frac{1}{0.00318 \frac{1}{K}} = 315 \text{ K} = 42 \text{ }^\circ\text{C}$$

Step 11: Check your work

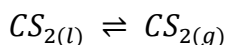
Does your answer seem reasonable?

The desired equilibrium constant is relatively close to the equilibrium constant at 25 °C, so it is reasonable that it will be achieved at a temperature close to 25 °C.

15.

- (a) *Equilibrium constants can be calculated from the standard free energy change for a reaction. Vapour pressure can be calculated from the equilibrium constant for evaporation.*

Step 1: Write a balanced chemical equation for the reaction (or phase change)



Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25 \text{ }^\circ\text{C} = 298.15 \text{ K}$$

Step 3: Calculate the standard free energy change for the reaction (or phase change)

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = [\Delta_f G^\circ(CS_{2(g)})] - [\Delta_f G^\circ(CS_{2(l)})]$$

$$\Delta_r G^\circ = \left(67.1 \frac{\text{kJ}}{\text{mol}}\right) - \left(64.6 \frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta_r G^\circ = 2.5 \frac{\text{kJ}}{\text{mol}}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K = -\frac{\left(2.5 \frac{\text{kJ}}{\text{mol}}\right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K = -1.0$$

$$K = e^{-1.0}$$

$$K = 0.4$$

Step 5: Use equilibrium constant expression to calculate vapour pressure

$$K = \frac{a_{CS_{2(g)}}}{a_{CS_{2(l)}}$$

$$K = \frac{\left(\frac{p_{CS_{2(g)}}}{1 \text{ bar}}\right)}{1}$$

$$p_{CS_{2(g)}} = K \cdot 1 \text{ bar} = 0.4 \text{ bar}$$

Step 6: Check your work

Does your answer seem reasonable? A positive standard free energy change should correspond to a small equilibrium constant (i.e. smaller than 1). Since CS₂ is a liquid at room temperature, its vapour pressure should be lower than atmospheric pressure at room temperature.

- (b) Normal boiling point is the temperature at which vapour pressure is 1 atm. That knowledge can be used to calculate the equilibrium constant at the boiling point.

From there, this becomes another “two temperatures; two equilibrium constants” question requiring the use of $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

Step 1: Determine activities for all reactants and products

$$a_{CS_2(l)} = 1 \qquad a_{CS_2(g)} = \frac{1 \text{ atm}}{1 \text{ bar}} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} = 1.01325$$

Step 2: Calculate the equilibrium constant for the pressures provided. This will be K_2 . (The equilibrium constant at 25 °C is K_1 . This was calculated in part (a).)

$$K_2 = \frac{a_{CS_2(g)}}{a_{CS_2(l)}}$$

$$K_2 = \frac{(1.01325)}{(1)} = 1.01325$$

Step 3: Match equilibrium constants to the corresponding temperature

$$T_1 = 298.15 \text{ K}$$

$$T_2 = ???$$

$$K_1 = 0.36$$

$$K_2 = 1.01325$$

Step 4: Calculate the standard enthalpy change for the reaction

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = [\Delta_f H^\circ(CS_2(g))] - [\Delta_f H^\circ(CS_2(l))]$$

$$\Delta_r H^\circ = \left(116.7 \frac{\text{kJ}}{\text{mol}}\right) - \left(89.0 \frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta_r H^\circ = +27.7 \frac{\text{kJ}}{\text{mol}} = +2.77 \times 10^4 \frac{\text{J}}{\text{mol}}$$

Step 5: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{1.01325}{0.36}\right) = \left(\frac{2.77 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}}}\right) \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{\ln\left(\frac{1.01325}{0.36}\right)(8.314 \ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}})}{2.77 \times 10^4 \frac{\text{J}}{\text{mol}}} = \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{1}{T_2} = \frac{1}{298.15 \text{ K}} - \frac{\ln\left(\frac{1.01325}{0.36}\right)(8.314 \ 462 \frac{\text{J}}{\text{mol}\cdot\text{K}})}{2.77 \times 10^4 \frac{\text{J}}{\text{mol}}}$$

$$\frac{1}{T_2} = \left(0.003 \ 354 \ 0 \frac{1}{\text{K}}\right) - \left(0.000 \ 307 \ \frac{1}{\text{K}}\right)$$

$$\frac{1}{T_2} = 0.003 \ 047 \ \frac{1}{\text{K}}$$

$$T_2 = \frac{1}{0.003 \ 047 \ \frac{1}{\text{K}}} = 328.2 \text{ K} = 55.0 \text{ }^\circ\text{C}$$

Step 6: Check your work

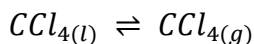
Does your answer seem reasonable?

The desired equilibrium constant is relatively close to the equilibrium constant at 25 °C, so it is reasonable that it will be achieved at a temperature close to 25 °C. Since we are told that CS₂ is a liquid at room temperature, its boiling point must be higher than room temperature.

16.

- (a) *Equilibrium constants can be calculated from the standard free energy change for a reaction. Vapour pressure can be calculated from the equilibrium constant for evaporation.*

Step 1: Write a balanced chemical equation for the reaction (or phase change)



Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25 \text{ }^\circ\text{C} = 298.15 \text{ K}$$

Step 3: Calculate the standard free energy change for the reaction (or phase change)

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = [\Delta_f G^\circ(CCl_4(g))] - [\Delta_f G^\circ(CCl_4(l))]$$

$$\Delta_r G^\circ = \left(-60.59 \frac{\text{kJ}}{\text{mol}}\right) - \left(-65.21 \frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta_r G^\circ = 4.62 \frac{\text{kJ}}{\text{mol}}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K = -\frac{\left(4.62 \frac{\text{kJ}}{\text{mol}}\right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K = -1.86$$

$$K = e^{-1.86}$$

$$K = 0.16$$

Step 5: Use equilibrium constant expression to calculate vapour pressure

$$K = \frac{a_{CCl_4(g)}}{a_{CCl_4(l)}}$$

$$K = \frac{\left(\frac{p_{CCl_4(g)}}{1 \text{ bar}}\right)}{1}$$

$$p_{CCl_4(g)} = K \cdot 1 \text{ bar} = 0.16 \text{ bar}$$

Step 6: Check your work

Does your answer seem reasonable? A positive standard free energy change should correspond to a small equilibrium constant (i.e. smaller than 1).

- (b) Liquid

Since the vapour pressure of CCl_4 is lower than atmospheric pressure at $25 \text{ }^\circ\text{C}$, this temperature must be lower than the boiling point of CCl_4 .

Alternatively, some students argued in favour of the liquid phase based on the calculated $\Delta_r G^\circ$. They stated that, because it was a positive value, the conversion of liquid to gas phase was not favoured at $25 \text{ }^\circ\text{C}$.

- (c) *This question is most easily answered using Raoult's Law. Begin by calculating the mole fraction of CCl_4 .*

Step 1: Calculate the moles of each species in solution

$$n_{\text{CCl}_4} = 250 \text{ g} \times \frac{1 \text{ mol}}{153.822 \text{ g}} = 1.63 \text{ mol CCl}_4$$

$$n_{\text{C}_6\text{H}_6} = 20.0 \text{ g} \times \frac{1 \text{ mol}}{78.113 \text{ g}} = 0.256 \text{ mol C}_6\text{H}_6$$

Step 2: Calculate the mole fraction of water in the solution

$$X_{\text{CCl}_4} = \frac{n_{\text{CCl}_4}}{(n_{\text{CCl}_4}) + (n_{\text{C}_6\text{H}_6})} = \frac{1.63 \text{ mol}}{(1.63 \text{ mol}) + (0.256 \text{ mol})} = 0.864$$

Step 3: Calculate the vapour pressure above the solution

$$p_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}} \cdot p^\circ_{\text{H}_2\text{O}} = (0.864)(0.16 \text{ bar}) = 0.13 \text{ bar}$$

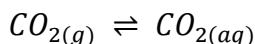
Step 4: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

The dissolved benzene lowers the vapour pressure of CCl_4 above the solution.

17. *This question is most easily answered using Henry's Law. Use the data in the first sentence to calculate the Henry's Law constant (k_H) for carbon dioxide. Use that constant to answer the question in the second sentence.*

Step 1: Write a balanced chemical equation for the reaction (or phase change)



Step 2: Calculate the Henry's Law constant for carbon dioxide

$$[\text{CO}_2] = k_H \cdot p_{\text{CO}_2}$$

$$k_H = \frac{[\text{CO}_2]}{p_{\text{CO}_2}} = \frac{(0.0351 \frac{\text{mol}}{\text{L}})}{(1.03 \text{ atm})} = 0.0341 \frac{\text{mol}}{\text{L}\cdot\text{atm}}$$

Step 3: Calculate solubility of carbon dioxide with a different partial pressure

$$[\text{CO}_2] = k_H \cdot p_{\text{CO}_2}$$

$$[\text{CO}_2] = \left(0.0341 \frac{\text{mol}}{\text{L}\cdot\text{atm}}\right) (2.24 \text{ atm})$$

$$[\text{CO}_2] = 0.0763 \frac{\text{mol}}{\text{L}}$$

Step 4: Check your work

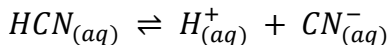
Does your answer seem reasonable? Are sig. fig. correct?

A higher partial pressure of carbon dioxide gas over the solution ought to result in a higher concentration of dissolved carbon dioxide. Since the pressure is approximately doubled, the concentration ought to be approximately doubled too.

18.

- (a) *Equilibrium constants can be calculated from the standard free energy change for a reaction.*
 K_a is the equilibrium constant for dissociation of H^+ from an acid.
 pK_a is readily calculated from K_a .

Step 1: Write a balanced chemical equation for the reaction (or phase change)



Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25.00\text{ }^\circ\text{C} = 298.15\text{ K}$$

Step 3: Calculate the standard free energy change for the reaction (or phase change)

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = [\Delta_f G^\circ(H^+_{(aq)}) + \Delta_f G^\circ(CN^-_{(aq)})] - [\Delta_f G^\circ(HCN_{(aq)})]$$

$$\Delta_r G^\circ = \left[\left(0 \frac{\text{kJ}}{\text{mol}} \right) + \left(166 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left(112 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta_r G^\circ = 54 \frac{\text{kJ}}{\text{mol}}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K = -\frac{\left(54 \frac{\text{kJ}}{\text{mol}} \right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (298.15\text{ K})} \times \frac{1000\text{ J}}{1\text{ kJ}}$$

$$\ln K = -22$$

$$K = e^{-22}$$

$$K = 3 \times 10^{-10}$$

Step 5: Calculate pK_a from K_a

$$pK_a = -\log(K_a) = -\log(3 \times 10^{-10}) = 9.5$$

Step 6: Check your work

Does your answer seem reasonable? A positive standard free energy change should correspond to a small equilibrium constant (i.e. smaller than 1). HCN is a weak acid, so it should have a pK_a value greater than 0. (Recall definition of strong vs. weak acid from CHEM 1000.)

- (b) *This is another “two temperatures; two equilibrium constants” question requiring the use of $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. As always, keeping organized is key to success.*

Step 1: Match equilibrium constants to the corresponding temperature

$$T_1 = 298.15\text{ K}$$

$$T_2 = 323.15\text{ K}$$

$$K_1 = 3 \times 10^{-10}$$

$$K_2 = ???$$

Step 2: Calculate the standard enthalpy change for the reaction

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = [\Delta_f H^\circ(H^+_{(aq)}) + \Delta_f H^\circ(CN^-_{(aq)})] - [\Delta_f H^\circ(HCN_{(aq)})]$$

$$\Delta_r H^\circ = \left[\left(0 \frac{\text{kJ}}{\text{mol}} \right) + \left(151 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left(105 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta_r H^\circ = +46 \frac{\text{kJ}}{\text{mol}} = +4.6 \times 10^4 \frac{\text{J}}{\text{mol}}$$

Step 3: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{3 \times 10^{-10}}\right) = \left(\frac{4.6 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}\right) \left(\frac{1}{298.15 \text{ K}} - \frac{1}{323.15 \text{ K}}\right)$$

$$\ln\left(\frac{K_2}{3 \times 10^{-10}}\right) = 1.4$$

$$\frac{K_2}{3 \times 10^{-10}} = e^{1.4}$$

$$\frac{K_2}{3 \times 10^{-10}} = 4$$

$$K_2 = (3 \times 10^{-10})(4)$$

$$K_2 = 1 \times 10^{-9}$$

Step 4: Check your work

Does your answer seem reasonable?

This reaction is endothermic ($\Delta_r H^\circ > 0$), so it is expected to have a larger equilibrium constant at the higher temperature.

Step 5: Answer the question!

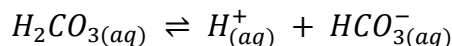
There was a verbal question attached to this calculation. It's easy to forget about that. Always re-read the question when you think you're done to make sure you answered everything!

HCN is a stronger acid at the higher temperature. The higher equilibrium constant means that it dissociates to a greater degree at 50.00 °C.

19.

- (a) *Equilibrium constants can be calculated from the standard free energy change for a reaction. K_a is the equilibrium constant for dissociation of H^+ from an acid.*

Step 1: Write a balanced chemical equation for the reaction (or phase change)



Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25.00\text{ }^\circ\text{C} = 298.15\text{ K}$$

Step 3: Calculate the standard free energy change for the reaction (or phase change)

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = [\Delta_f G^\circ(H_{(aq)}^+) + \Delta_f G^\circ(HCO_{3(aq)}^-)] - [\Delta_f G^\circ(H_2CO_{3(aq)})]$$

$$\Delta_r G^\circ = \left[\left(0 \frac{\text{kJ}}{\text{mol}} \right) + \left(-586.8 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left(-623.1 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta_r G^\circ = 36.3 \frac{\text{kJ}}{\text{mol}}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K = -\frac{\left(36.3 \frac{\text{kJ}}{\text{mol}} \right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (298.15\text{ K})} \times \frac{1000\text{ J}}{1\text{ kJ}}$$

$$\ln K = -14.6$$

$$K = e^{-14.6}$$

$$K = 4 \times 10^{-7}$$

Step 5: Check your work

Does your answer seem reasonable? A positive standard free energy change should correspond to a small equilibrium constant (i.e. smaller than 1). H_2CO_3 is a weak acid, so it should have a K_a value less than 1.

- (b) $\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$

$$\Delta_r H^\circ = [\Delta_f H^\circ(H_{(aq)}^+) + \Delta_f H^\circ(HCO_{3(aq)}^-)] - [\Delta_f H^\circ(H_2CO_{3(aq)})]$$

$$\Delta_r H^\circ = \left[\left(0 \frac{\text{kJ}}{\text{mol}} \right) + \left(-689.9 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left(-699.7 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta_r H^\circ = +9.8 \frac{\text{kJ}}{\text{mol}}$$

Since $\Delta_r H^\circ > 0$, this reaction is endothermic, so increasing the temperature will favour the forward reaction. This corresponds to an increase in the equilibrium constant (K_a) and a strengthening of the acid (since more H^+ is present at equilibrium).