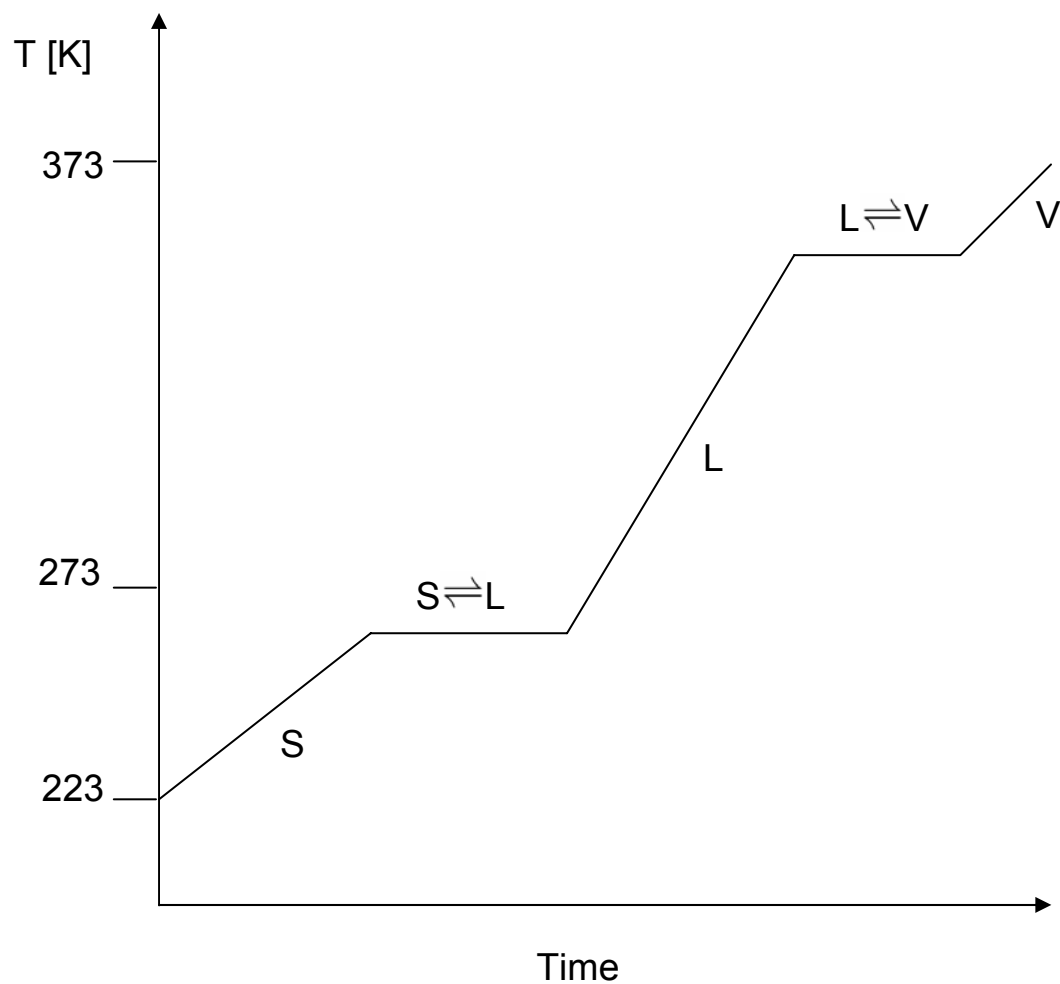
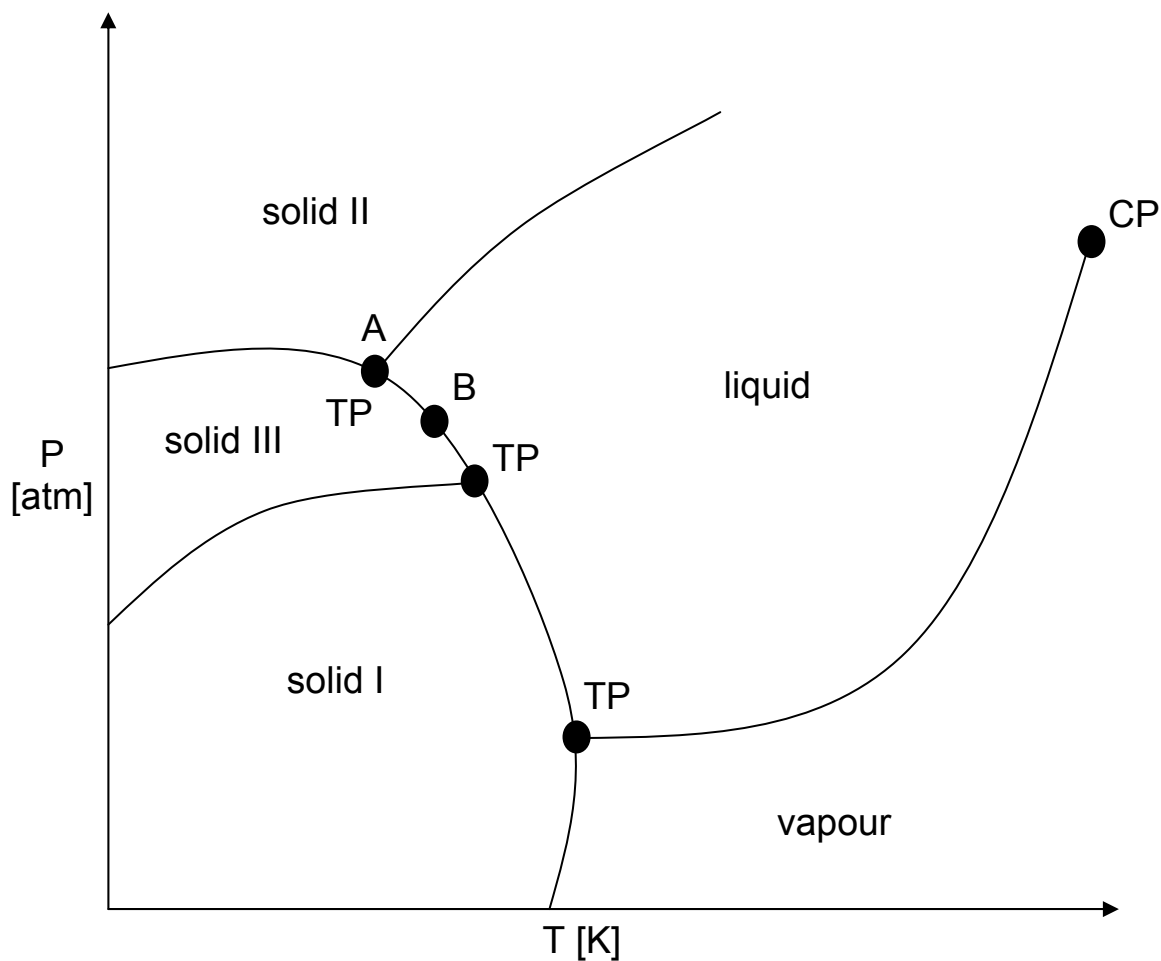


1. A substance has the following properties: boiling point = 75°C and melting point = -15°C . Sketch a heating curve for the substance from -50 to 100°C in the diagram shown below. Clearly label the phases present at each individual step (five steps).

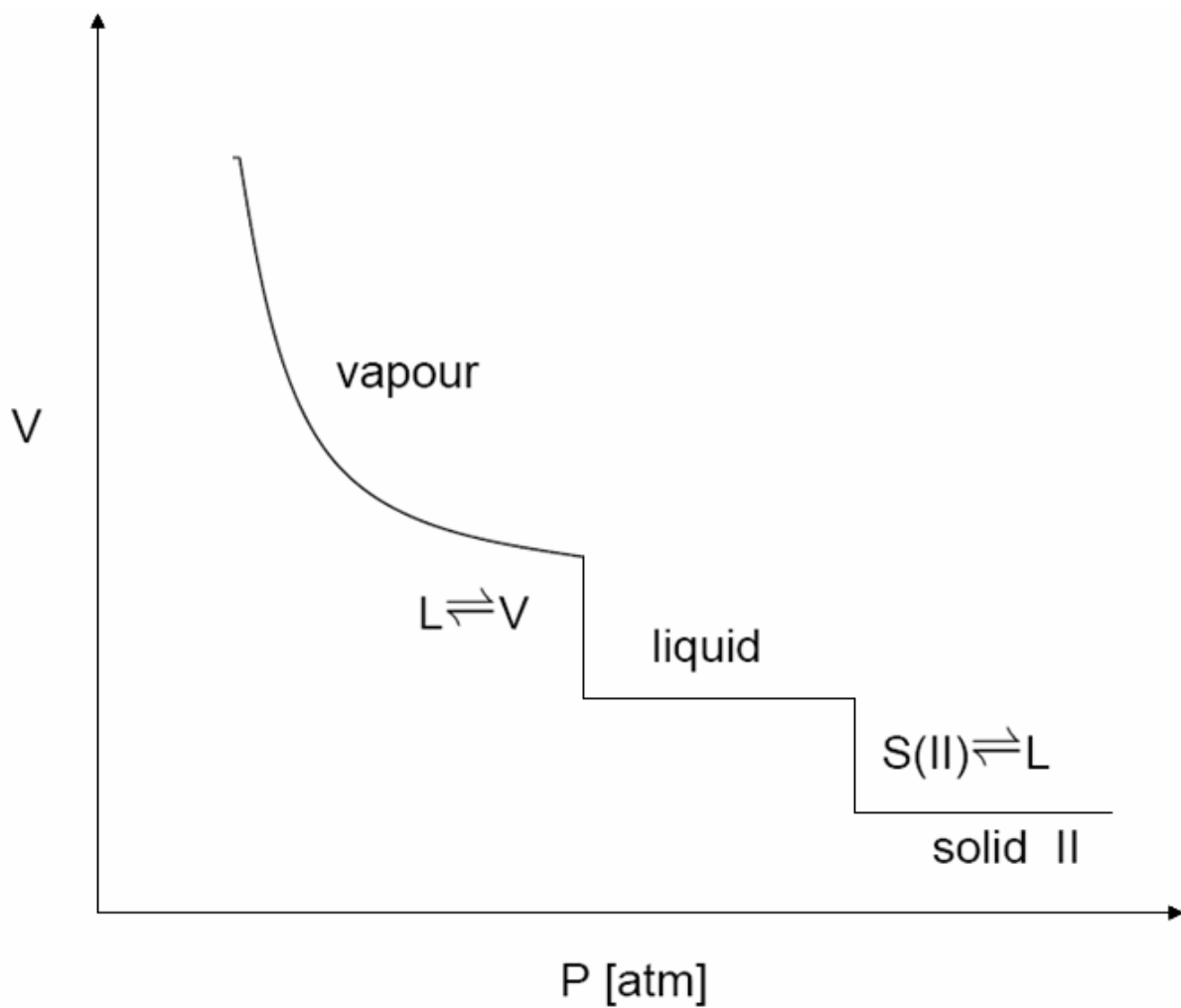


2. A phase diagram for an unknown substance is shown below. This substance has a vapour and liquid phase, and three solid phases (solid I, II and III). At point A on the diagram, solid III, solid II and the liquid phase are in equilibrium. Solid II is denser than solid III.



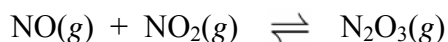
- (a) Label the states present in each of the five regions of the phase diagram.
- (b) Label all triple points with TP and the critical point with CP.
- (c) Which phase present at point B has the higher density? (**Liquid**)

- (d) Sketch (not to scale) on the axis below the effect of decreasing pressure on the volume of the substance along the dashed line on the phase diagram on page 2.



3. Assume that all gases are ideal. For ideal gases, $PV = nRT$, and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

One possible way to make dinitrogen trioxide (N_2O_3) is through the following reaction:



At 298.15°K , the basic thermodynamic quantities are given below:

Substance	$\Delta H_f^\circ (\text{kJ mol}^{-1})$	$S^\circ (\text{J mol}^{-1} \text{K}^{-1})$	$\Delta G_f^\circ (\text{kJ mol}^{-1})$
$\text{NO}(g)$	91.3	210.8	87.6
$\text{NO}_2(g)$	33.2	240.1	51.3
$\text{N}_2\text{O}_3(g)$	82.8	314.6	

- (a) What is the heat of reaction under constant pressure at 298.15°K under standard conditions?

$$q_p = \underline{-41.7 \text{ kJ}}$$

$$\begin{aligned} q_p &= \Delta H^\circ = \sum_{\text{moles}} \Delta H_f^\circ(\text{products}) - \sum_{\text{moles}} \Delta H_f^\circ(\text{reactants}) \\ &= 82.8 - (91.3 + 33.2) = -41.7 \text{ kJ} \end{aligned}$$

- (b) Calculate ΔS° , ΔE° , and ΔG° for this reaction at 298.15°K ?

$$\Delta S^\circ = \underline{-136.3 \text{ J/K}} \quad \Delta E^\circ = \underline{-39.2 \text{ kJ}} \quad \Delta G^\circ = \underline{-1.1 \text{ kJ}}$$

$$\begin{aligned} \Delta S^\circ &= \sum_{\text{moles}} S^\circ(\text{products}) - \sum_{\text{moles}} S^\circ(\text{reactants}) \\ &= 314.6 - (210.8 + 240.1) = -136.3 \text{ J K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -41.7 - 298.15 \times (-136.3 \times 10^{-3}) = -1.1 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta E^\circ &= \Delta H^\circ - \Delta(PV) \\ &= \Delta H^\circ - \Delta(nRT) \\ &= \Delta H^\circ - (\Delta n)RT \\ &= -41.7 - (-1) \times 8.314 \times 298.15 \times 10^{-3} = -39.2 \text{ kJ} \end{aligned}$$

- (c) Evaluate the standard Gibbs free energy of formation, ΔG_f° , of $N_2O_3(g)$ at 298.15°K.

$$\Delta G_f^\circ(N_2O_3) = \underline{137.8 \text{ kJ/mol}}$$

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

$$-1.1 = \Delta G_f^\circ(N_2O_3) - (87.6 + 51.3)$$

$$\Delta G_f^\circ(N_2O_3) = 137.8 \text{ kJ mol}^{-1}$$

- (d) Evaluate the equilibrium constant, K, at 298.15°K.

$$K = \underline{1.6}$$

$$\Delta G^\circ = -RT \cdot \ln K$$

$$\ln K = -\Delta G^\circ / (RT)$$

$$\ln K = -(-1.1) / (8.314 \times 298.15 \times 10^{-3}) \approx 0.44$$

$$K \approx e^{0.44} \approx 1.6$$

- (e) Write an expression for the equilibrium constant in terms of activities and in terms of partial pressures.

$$K = \frac{a_{N_2O_3(g)}}{[a_{NO(g)} \cdot a_{NO_2(g)}]}$$

$$\approx \frac{P_{N_2O_3(g)}}{[P_{NO(g)} \cdot P_{NO_2(g)}]}$$

- (f) Could this reaction be used to mass produce N_2O_3 at 298.15°K? **Give reasoning for your answer.**

Yes ☺ or No _____

Yes.

Because $\Delta G^\circ = -1.1 \text{ kJ} < 0$.

- (g) Will increasing the temperature favour the production of N_2O_3 ? **Give reasoning for your answer.**

Yes _____ or No ☺

No.

$$\Delta H^\circ = -41.7 \text{ kJ} < 0$$

decreasing T favours exothermic reaction.

- (h) If a chemical factory operating under standard conditions is built in a desert near the equator in Australia, where the temperature stays above 35°C during the entire year, will N_2O_3 be produced spontaneously by using this reaction? Assume that ΔS° and ΔH° do not change with the temperature. **Give reasoning for your answer.**

Yes _____ or No ☒ _____

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0$ for spontaneous process.

$$\Delta H^\circ < T\Delta S^\circ, \Delta S^\circ = -136.3 \text{ J K}^{-1} < 0$$

$T < \Delta H^\circ / \Delta S^\circ = T_0$ for spontaneous process.

$$T_0 = \Delta H^\circ / \Delta S^\circ = -41.7 / (-136.3 \times 10^{-3}) \approx 305.9^\circ\text{K} = 32.8^\circ\text{C}$$

When $T = 35^\circ\text{C} > T_0 = 32.8^\circ\text{C}$, $\Delta G^\circ > 0$

Thus, non-spontaneous.

Alternatively, use the van't Hoff equation and equilibrium constant.

$\Delta G^\circ = -RT \cdot \ln K < 0$ for spontaneous process

Hence, $\ln K = -\Delta G^\circ / (RT) > 0$ for spontaneous process

For $\ln K > 0$, $K > 1$ for spontaneous process

Let's calculate K_2 at $T_2 = 35^\circ\text{C} = 308.15^\circ\text{K}$,
with K_1 at $T_1 = 25^\circ\text{C} = 298.15^\circ\text{K}$ and $\Delta H^\circ = -41.7 \text{ kJ}$,
using the van't Hoff equation:

$$\ln(K_1/K_2) = (\Delta H^\circ / R) \times (T_2^{-1} - T_1^{-1})$$

$$\ln(K_1/K_2) = -41.7 / (8.314 \times 10^{-3}) \times (308.15^{-1} - 298.15^{-1}) \approx 0.55$$

$$K_1/K_2 \approx e^{0.55} \approx 1.73$$

$$K_2 \approx K_1 / 1.73 \approx 1.6 / 1.73 \approx 0.9 < 1$$

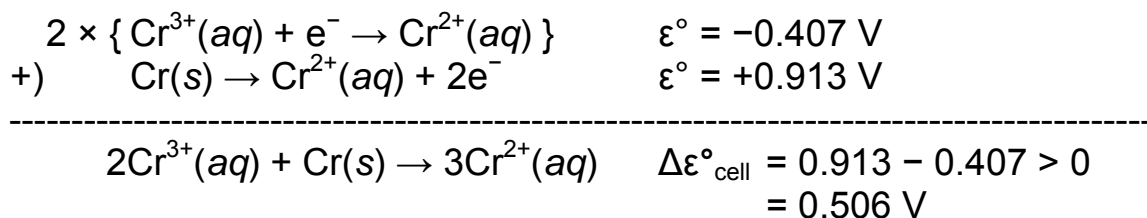
Thus, non-spontaneous.

4. Consider the galvanic cell based on the following half-reactions at 25°C



- (a) Write the overall cell reaction in the direction of spontaneous change.

$\Delta\varepsilon^{\circ}_{\text{cell}}$ has to be positive for spontaneous change. This requires that the second equation be subtracted from the first that has to be multiplied by 2 to balance electrons.



- (b) Calculate the standard cell potential $\Delta\varepsilon^{\circ}_{\text{cell}}$ and ΔG°

$$\Delta\varepsilon^{\circ}_{\text{cell}} = \underline{0.506 \text{ V}} \quad \Delta G^{\circ} = \underline{-97.7 \text{ kJ}}$$

$$\Delta\varepsilon^{\circ}_{\text{cell}} = 0.913 - 0.407 = 0.506 \text{ V}$$

$$\begin{aligned} \Delta G^{\circ} &= -nF\Delta\varepsilon^{\circ}_{\text{cell}} \\ &= -2 \times 96500 \times 0.506 = -97658 \text{ J} \approx -97.7 \text{ kJ} \end{aligned}$$

- (c) Calculate the cell potential $\Delta\varepsilon_{\text{cell}}$ when the concentration of $\text{Cr}^{2+}(\text{aq})$ and $\text{Cr}^{3+}(\text{aq})$ are both 0.001 M.

$$\begin{aligned} \Delta\varepsilon_{\text{cell}} &= \Delta\varepsilon^{\circ}_{\text{cell}} - \frac{RT \cdot \ln Q}{nF} \\ &= 0.506 - \frac{[8.314 \times 298.15]}{(2 \times 96500)} \times \ln \left\{ \frac{[\text{Cr}^{2+}]^3}{[\text{Cr}^{3+}]^2} \right\} \\ &= 0.506 - \frac{[8.314 \times 298.15]}{(2 \times 96500)} \times \ln(0.001) \\ &\approx 0.506 - (-0.0887) \approx 0.595 \text{ V} \end{aligned}$$

- (d) Qualitatively (that is increase, decrease, or no change), what happens to the cell potential of a cell operating under standard conditions, when some NaOH solution is added to the compartment containing Cr(s) and $\text{Cr}^{2+}(\text{aq})$? The compound $\text{Cr}(\text{OH})_2$ precipitates: it is a sparingly soluble substance. **Provide a brief explanation of your choice.**

Increase ☺ or Decrease _____ or No Change _____

$$\Delta \epsilon_{\text{cell}} = \Delta \epsilon^{\circ}_{\text{cell}} - RT \cdot \ln Q / (nF)$$

$$Q = [\text{Cr}^{2+}]^3 / [\text{Cr}^{3+}]^2$$

The removal of $\text{Cr}^{2+}(\text{aq})$ as $\text{Cr}(\text{OH})_2(\text{s})$ will decrease $[\text{Cr}^{2+}]$, causing Q to decrease. Then, $\ln Q$ will decrease, $-RT \cdot \ln Q / (nF)$ will increase accordingly, and $\Delta \epsilon_{\text{cell}}$ will increase as a result.

- (e) Given that the standard cell potential goes down on raising the temperature, what is the sign of the enthalpy change for the cell reaction at 25°C? **Provide a brief explanation of your choice.**

Plus _____ or Minus ☺

Let's use the van't Hoff equation for this question.

We are given $T_1 < T_2$ and $\Delta \epsilon^{\circ}_1 > \Delta \epsilon^{\circ}_2$, with

T_1	K_1	$\Delta \epsilon^{\circ}_1$
T_2	K_2	$\Delta \epsilon^{\circ}_2$

van't Hoff equation: $\ln(K_1/K_2) = (\Delta H^{\circ}/R) \times (T_2^{-1} - T_1^{-1})$

Also, $\Delta \epsilon^{\circ}_1 = RT_1 \cdot \ln K_1 / (nF)$, $\Delta \epsilon^{\circ}_2 = RT_2 \cdot \ln K_2 / (nF)$,

$\ln(K_1/K_2) = \ln K_1 - \ln K_2 = (nF/R) \times [\Delta \epsilon^{\circ}_1/T_1 - \Delta \epsilon^{\circ}_2/T_2]$

Hence, $nF \cdot (\Delta \epsilon^{\circ}_1/T_1 - \Delta \epsilon^{\circ}_2/T_2) = \Delta H^{\circ} \cdot (T_2^{-1} - T_1^{-1})$ (☼)

$T_1 < T_2$, then $T_1^{-1} > T_2^{-1}$, thus $(T_2^{-1} - T_1^{-1}) < 0$

$T_1^{-1} > T_2^{-1}$ and $\Delta \epsilon^{\circ}_1 > \Delta \epsilon^{\circ}_2$, thus $(\Delta \epsilon^{\circ}_1/T_1 - \Delta \epsilon^{\circ}_2/T_2) > 0$

Now, look at Eq. (☼), all the terms on the LHS are positive, the term in the brackets on the RHS is negative. Therefore, ΔH° must be negative: $\Delta H^{\circ} < 0$.