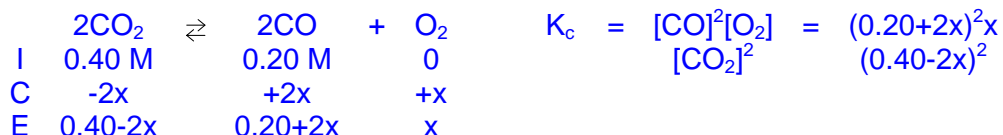


1. For the equilibrium below, $K_c = 2.0 \times 10^{-6}$. What is the equilibrium concentration of oxygen (in moles/L) if 0.20 mol CO_2 and 0.10 mol CO were initially placed into an evacuated 0.50 L vessel and the system is allowed to come to equilibrium? (9 points)



Since we have zero O_2 initially, we know we cannot be at equilibrium so we must use an ICE table or some other approach to find equilibrium concentrations.

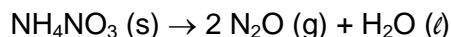


Without some simplification, we will need to solve a third order polynomial. Can we simplify? Since K is small, we would not expect the reaction to proceed very far to the right. Also, the presence of CO initially will further impede the reaction. So, we expect x to be small. Lets assume $x \ll 0.20$. If this is so, the K_c expression changes.

$$K_c = \frac{(0.20+2x)^2x}{(0.40-2x)^2} = \frac{(0.20)^2x}{(0.40)^2}$$

After rearranging we find that $x = K_c(0.40)^2/(0.20)^2 = 8.0 \times 10^{-6}$. So, $[\text{O}_2] = 8.0 \times 10^{-6}\text{M}$. Was our assumption OK? $0.20 - 0.0000080 = 0.1999920$, which to the correct number of sig figs is indistinguishable from 0.20, so our assumption is fine. We could have used a calculator or computer to solve the third order polynomial. Doing so on my calculator gave a value for x of 7.998×10^{-6} .

2. Solid ammonium nitrate can decompose to dinitrogen oxide gas and liquid water by the reaction below. What is the ΔG° at 298K? At what temperature, if any, does spontaneity of the reaction change? (9 points)



Species	ΔH°_f (kJ/mol)	S°_f (J/mol)
$\text{NH}_4\text{NO}_3(\text{s})$	-365.6	151.1
$\text{N}_2\text{O}(\text{g})$	+82.05	219.9
$\text{H}_2\text{O}(\ell)$	-285.8	69.91

For my incorrectly balanced reaction above:

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

$$\Delta H^\circ = 2\Delta H^\circ_f(\text{N}_2\text{O}) + \Delta H^\circ_f(\text{H}_2\text{O}) - [\Delta H^\circ_f(\text{NH}_4\text{NO}_3)]$$

$$\Delta H^\circ = [2(+82.05) + (-285.8)] - [(-365.6)]\text{kJ}$$

$$\Delta H^\circ = +243.9 \text{ kJ}$$

$$\Delta S^\circ = 2\Delta S^\circ_f(\text{N}_2\text{O}) + \Delta S^\circ_f(\text{H}_2\text{O}) - [\Delta S^\circ_f(\text{NH}_4\text{NO}_3)]$$

$$\Delta S^\circ = [2(219.9) + (69.91)] - [(151.1)]\text{J/K}$$

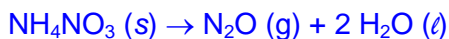
$$\Delta S^\circ = +358.6 \text{ J/K}$$

$$\Delta G^\circ = 243.9 \text{ kJ/mol} - 298 \text{ K}(0.3586 \text{ kJ/mol K}) = \mathbf{+137.0 \text{ kJ}}$$

To find the temperature where spontaneity changes, set $\Delta G^\circ = 0$ and solve for T :

$$T = \Delta H^\circ / \Delta S^\circ = 243.9 / 0.3586 = \mathbf{680 \text{ K}}$$

For the correctly balanced reaction:



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

$$\Delta H^\circ = \Delta H_f^\circ(\text{N}_2\text{O}) + 2\Delta H_f^\circ(\text{H}_2\text{O}) - [\Delta H_f^\circ(\text{NH}_4\text{NO}_3)]$$

$$\Delta H^\circ = [(+82.05) + 2(-285.8)] - [(-365.6)]\text{kJ}$$

$$\Delta H^\circ = -123.95 \text{ kJ}$$

$$\Delta S^\circ = \Delta S_f^\circ(\text{N}_2\text{O}) + 2\Delta S_f^\circ(\text{H}_2\text{O}) - [\Delta S_f^\circ(\text{NH}_4\text{NO}_3)]$$

$$\Delta S^\circ = [(219.9) + 2(69.91)] - [(151.1)]\text{J/K}$$

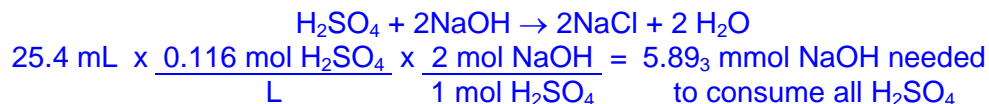
$$\Delta S^\circ = +208.6 \text{ J/K}$$

$$\Delta G^\circ = -123.95 \text{ kJ/mol} - 298 \text{ K}(0.2086 \text{ kJ/mol K}) = \mathbf{-186.1 \text{ kJ}}$$

Since ΔH° is negative and ΔS° is positive and since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, there is no temperature where the reaction is nonspontaneous. Since T is always positive, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ will be negative at all temperatures when ΔH° is negative and ΔS° is positive.

3. 25.4 mL of 0.116 M H_2SO_4 is mixed with 22.4 mL of 0.282 M NaOH. What is the pH of the resulting solution? (7 points)

This is a strong acid/strong base reaction. The pH will be determined by what's left after the acid and base react.



$$22.4 \text{ mL} \times \frac{0.282 \text{ mol H}_2\text{SO}_4}{\text{L}} = 6.31_7 \text{ mmol NaOH present}$$

So, H_2SO_4 is the limiting reagent, some NaOH will be left over, how much?

$$(6.31_9 - 5.89_3) = 0.424 \text{ mmol}$$

This will dissociate completely to give 0.426 mmol of OH^- or an $[\text{OH}^-]$ of:

$$\frac{0.424 \text{ mmol OH}^-}{(25.4+22.4)\text{mL}} = 8.87_0 \times 10^{-3}\text{M}$$

$$\text{pOH} = -\log(8.87_0 \times 10^{-3}) = 2.05_2$$

$$\mathbf{\text{pH} = 14 - \text{pOH} = 11.95}$$

