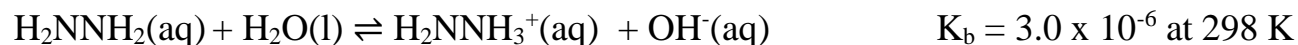


1. Hydrazine ( $\text{H}_2\text{NNH}_2$ ) was used as a rocket fuel in World War II. Hydrazine acts as a base as described by the reaction below:



- a) Calculate  $\Delta G^\circ$ , in kJ, for the reaction at 298 K.

$$\begin{aligned} \Delta G^\circ &= -RT \ln K = -1 \text{ mol} \times (8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln(3.0 \times 10^{-6})) \\ &= 31509 \text{ J} = 32 \text{ kJ} \end{aligned}$$

- b) What is the value of  $\Delta G_{\text{rxn}}$  at equilibrium?

**$\Delta G_{\text{rxn}} = 0$  at equilibrium**

- c) What is the value of  $\Delta G_{\text{rxn}}$ , in kJ, at 298 K when  $[\text{OH}^-] = 2.37 \times 10^{-6} \text{ M}$ ,  $[\text{H}_2\text{NNH}_3^+] = 7.89 \times 10^{-3} \text{ M}$ ,  $[\text{H}_2\text{O}] = 55.5 \text{ M}$ , and  $[\text{H}_2\text{NNH}_2] = 0.061 \text{ M}$ ?

**Water has an activity of 1 because it is a pure liquid.**

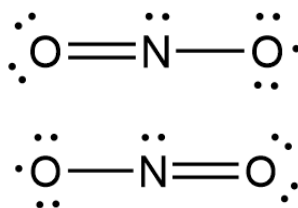
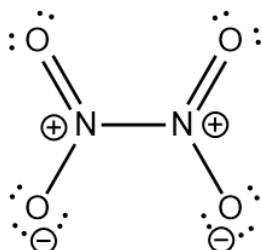
$$\Delta G_{\text{rxn}} = \Delta G^\circ + RT \ln Q$$

$$\begin{aligned} \Delta G_{\text{rxn}} &= 31509 \text{ J} + 1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \\ &\quad \times 298 \text{ K} \times \ln \left[ \frac{(2.37 \times 10^{-6})(7.89 \times 10^{-3})}{0.061} \right] \\ &= 31509 \text{ J} - 37163 \text{ J} = -5653.8 \text{ J} = -5.65 \text{ kJ} \end{aligned}$$

2. Consider the reaction:  $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

$\text{NO}_2$  is a dark brown colour and  $\text{N}_2\text{O}_4$  is colourless. ([www.youtube.com/watch?v=oC3klPMRnwo](http://www.youtube.com/watch?v=oC3klPMRnwo))

- a) Draw the best Lewis structures of the reactant and the product ( $\text{NO}_2$  has an odd number of valence electrons called a radical species) and write the equilibrium expression for the reaction.



$$K = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2}$$

- b) When an equilibrium mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in a sealed tube is placed in an ice bath, what colour change is observed? What does this tell you about the extent of the reaction?

**The gas inside the tube changes colour from brown to colourless (light brown).**

- c) Is the reaction exothermic or endothermic? Briefly explain.

**The reaction is exothermic.**

**First, no bonds are being broken and one bond is being formed. Bond breaking requires energy (endothermic), bond forming releases energy (exothermic).**

**Second, when the temperature decreases, formation of the products is favored. Consider the equilibrium:**



**A decrease in temperature causes the equilibrium to shift to the right according to Le Chatelier's principle. In other words, heat will be produced to compensate for the decrease in temperature. This is what is observed, therefore the reaction is exothermic.**

**Third. Decreasing temperature increases the equilibrium constant (product formation is favored). Therefore, a graph of  $\ln K$  vs.  $1/T$  will have a positive slope since  $\ln K$  increases when  $K$  increases and  $1/T$  increases as  $T$  decreases. According to the van't Hoff equation, if a plot of  $\ln K$  vs.  $1/T$  has a positive slope, the reaction is exothermic.**

3. **Good question.** Glucose and fructose phosphates are found at equilibrium ( $\text{Glu(aq)} \rightleftharpoons \text{Fru(aq)}$ ) in metabolic pathways.  $\Delta G^\circ$  at 298 K is 1.67 kJ for this reaction.

a) Determine the equilibrium constant for the reaction as written at 298 K.

$$\Delta G^\circ = -RT \ln K = -1 \text{ mol} \times (8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln K) = 1.67 \text{ kJ}$$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = \exp \left[ \frac{-1.67 \text{ kJ}}{1 \text{ mol} \times (8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K})} \right] = e^{-0.674} = 0.51$$

b) What is the composition (%Glu and %Fru) at equilibrium at 298K?

	Glu(aq)	$\rightleftharpoons$	Fru(aq)
[initial] mol/L	1		0
[equilib] mol/L	1-x		x

$$K = \frac{[\text{Fru}]}{[\text{Glu}]} = \frac{x}{1-x} = 0.51$$

$$x = 0.51 - 0.51x \quad \rightarrow \quad 1.51x = 0.51$$

$$x = \frac{0.51}{1.51} = 0.34$$

$$\% \text{Fru} = x \times 100\% = 34\%$$

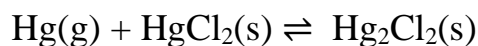
$$\% \text{Glu} = (1 - x) \times 100\% = 66\%$$

**Alternatively, a more direct calculation gives**

$$\text{fraction of Glu} = \frac{[\text{Glu}]}{[\text{Fru}] + [\text{Glu}]} = \frac{1}{\frac{[\text{Fru}]}{[\text{Glu}] + 1}} = \frac{1}{K+1} = \frac{1}{0.51+1} = 0.66$$

**so that %Glu = 66% and %Fru = 34%.**

4.  $\text{Hg}_2\text{Cl}_2$  was widely used to make reference electrodes, known as calomel electrodes, and can be produced by the reaction



	<b>Hg(g)</b>	<b>HgCl<sub>2</sub>(s)</b>	<b>Hg<sub>2</sub>Cl<sub>2</sub>(s)</b>
$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	61.4	-224.3	-265.4
$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	31.8	-178.6	-210.7
$S_m^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	175.0	146.0	191.6

Some standard thermodynamic data (measured at 298 K) is given in the table for these species.

- a) Write out the equilibrium expression in terms of activities.

$$K = \frac{a(\text{Hg}_2\text{Cl}_2)}{a(\text{Hg})a(\text{HgCl}_2)}$$

- b) Determine the temperature at which the equilibrium pressure is 1.00 bar.

$$\begin{aligned}\Delta H^0 &= [1 \text{ mol} \times (-265.4 \text{ kJ mol}^{-1})] \\ &\quad - [1 \text{ mol} \times (61.4 \text{ kJ mol}^{-1}) + 1 \text{ mol} \times (-224.3 \text{ kJ mol}^{-1})] \\ &= -102.5 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^0 &= [1 \text{ mol} \times (191.6 \text{ J mol}^{-1} \text{ K}^{-1})] \\ &\quad - [1 \text{ mol} \times (175.0 \text{ J mol}^{-1} \text{ K}^{-1}) + 1 \text{ mol} \times (146.0 \text{ J mol}^{-1} \text{ K}^{-1})] \\ &= -129.4 \text{ J K}^{-1}\end{aligned}$$

These are values at 298 K but approximate them as independent of temperature. Since  $\text{Hg}_2\text{Cl}_2$  and  $\text{HgCl}_2$  are solids, their activities are taken as unity, while  $\text{Hg(g)}$  is a gas, whose activity can be approximated as the pressure. When  $P(\text{Hg}) = 1.00 \text{ bar}$ ,  $K = 1$ , from a) above, so that

$$\Delta G^0 = -RT \ln K = -RT \ln 1 = 0 = \Delta H^0 - T\Delta S^0$$

$$T = \frac{\Delta H^0}{\Delta S^0} = \frac{(-102.5 \text{ kJ}) \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right)}{-129.4 \text{ J K}^{-1}} = 792 \text{ K}$$

- c) Determine the equilibrium constant at 1300 K

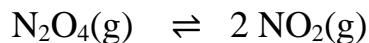
$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = (-102.5 \text{ kJ}) - (1300 \text{ K})(-0.1294 \text{ kJ K}^{-1}) = 65.7 \text{ kJ}$$

$$K = \exp\left(\frac{-\Delta G^0}{RT}\right) = \exp\left(\frac{-65700 \text{ J}}{1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 1300 \text{ K}}\right) = 2.3 \times 10^{-3}$$

- d) How will the following changes impact the **spontaneity** of the forward reaction?

A. the pressure of $\text{Hg(g)}$ is increased:	<b>Increase</b>	Decrease	Remain the same
B. the amount of $\text{Hg}_2\text{Cl}_2\text{(s)}$ is increased:	Increase	Decrease	<b>Remain the same</b>

5. **Good question.** Consider the equilibrium below



and the thermodynamic data (measured at 298 K) in the table.

	$\text{N}_2\text{O}_4(\text{g})$	$\text{NO}_2(\text{g})$
$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	9.66	33.84
$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	98.28	51.84
$S_m^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	304.3	240.45

- a) At what temperature will an equilibrium mixture contain one bar pressure EACH of  $\text{N}_2\text{O}_4(\text{g})$  and  $\text{NO}_2(\text{g})$ ?

$$\Delta H^0 = [2 \text{ mol} \times (33.84 \text{ kJ mol}^{-1})] - [1 \text{ mol} \times (9.66 \text{ kJ mol}^{-1})] = 58.02 \text{ kJ}$$

$$\Delta S^0 = [2 \text{ mol} \times (240.45 \text{ J mol}^{-1} \text{ K}^{-1})] - [1 \text{ mol} \times (304.3 \text{ J mol}^{-1} \text{ K}^{-1})] = 176.6 \text{ J K}^{-1}$$

**These are values at 298 K but approximate them as independent of temperature.  
Now use the equilibrium expression and its relationship with Gibbs' energy:**

$$K = \frac{P(\text{NO}_2)^2}{P(\text{N}_2\text{O}_4)} = \frac{(1)^2}{1} = 1$$

$$\Delta G^0 = -RT \ln K = -RT \ln 1 = 0 = \Delta H^0 - T\Delta S^0$$

$$T = \frac{\Delta H^0}{\Delta S^0} = \frac{58.02 \times 10^3 \text{ J}}{176.6 \text{ J K}^{-1}} = 328.4 \text{ K}$$

- b) At what temperature will an equilibrium mixture at a total pressure of 1.00 bar contain twice as much  $\text{NO}_2$  as  $\text{N}_2\text{O}_4$ ?

$$P(\text{Total}) = 1 \text{ bar and } P(\text{NO}_2) = 2 \times P(\text{N}_2\text{O}_4).$$

**Therefore,  $P(\text{NO}_2) = 0.6667 \text{ bar}$  and  $P(\text{N}_2\text{O}_4) = 0.3333 \text{ bar}$ , and following a similar procedure as used in a) gives**

$$K = \frac{P(\text{NO}_2)^2}{P(\text{N}_2\text{O}_4)} = \frac{(0.6667)^2}{0.3333} = 1.333$$

$$\Delta G^0 = -RT \ln K = \Delta H^0 - T\Delta S^0$$

**Now solve for T**

$$T = \frac{\Delta H^0}{-R \ln K + \Delta S^0} = \frac{(58.02 \text{ kJ}) \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right)}{-1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln(1.333) + 176.6 \text{ J K}^{-1}} = 333 \text{ K}$$

- c) At what temperature will an equilibrium mixture at a total pressure of 10.0 bar contain twice as much  $\text{NO}_2$  as  $\text{N}_2\text{O}_4$ ?

$$P(\text{Total}) = 10 \text{ bar and } P(\text{NO}_2) = 2 \times P(\text{N}_2\text{O}_4).$$

Therefore,  $P(\text{NO}_2) = 6.666 \text{ bar}$  and  $P(\text{N}_2\text{O}_4) = 3.33 \text{ bar}$ , and again repeating the same procedure used in b) gives

$$K = \frac{P(\text{NO}_2)^2}{P(\text{N}_2\text{O}_4)} = \frac{(6.666)^2}{3.333} = 13.33$$

$$\Delta G^0 = -RT \ln K = \Delta H^0 - T\Delta S^0$$

Now, solve for T

$$T = \frac{\Delta H^0}{-R \ln K + \Delta S^0} = \frac{(58.02 \text{ kJ}) \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right)}{-1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln(13.33) + 176.6 \text{ J K}^{-1}} = 374 \text{ K}$$

- d) Rationalize the results from parts (b) and (c) using Le Chatelier's principle.

The reaction is endothermic, so an increase in the value of K as calculated in parts (a)-(c) should result from an increase in system temperature, as shown by the increasing temperatures calculated in those sections.

- e) To what temperature must the system be raised to make the equilibrium constant equal to 1000?

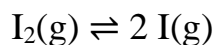
The van't Hoff equation can be used to predict the equilibrium constant at a different temperature, once it is known at one temperature. From part a) we know  $K = 1$  when  $T = 328.4 \text{ K}$  so that

$$\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \left( \frac{1000}{1} \right) = -\frac{58.02 \text{ kJ}}{1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{T_2} - \frac{1}{328.4 \text{ K}} \right)$$

Solving for  $T_2$  gives 486.6 K which is the temperature needed to increase the rate constant to 1000.

6. **Good Question.** Use the data below to graphically determine  $\Delta H^\circ$  and  $\Delta S^\circ$  for the gas-phase dissociation of molecular iodine:



T (K)	872	973	1073	1173
Equilibrium Constant	$1.8 \times 10^{-4}$	$1.8 \times 10^{-3}$	$1.08 \times 10^{-2}$	0.0480

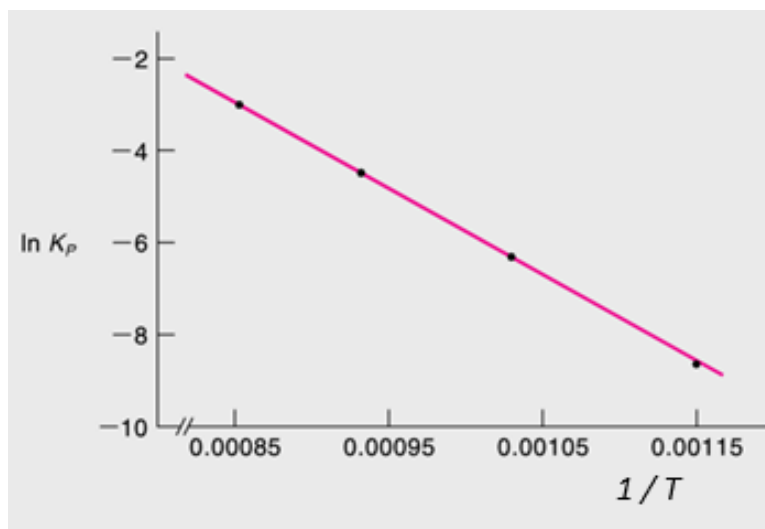
Plot  $\ln K$  vs.  $1/T$  (on right)

Slope =  $-\Delta H^\circ/R \sim -18800 \text{ K}$

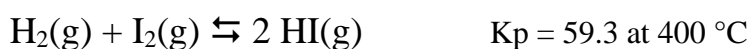
y-intercept =  $\Delta S^\circ/R \sim 13$

$\Delta H^\circ = 1.56 \times 10^2 \text{ kJ}$

$\Delta S^\circ = 108 \text{ J K}^{-1}$



7. Hydroiodic acid is produced commercially for lab use in a chemical plant reactor. The reactor operates at 400 °C, housing the following equilibrium reaction:



If the initial partial pressures of  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$  are each 2.50 bar, what is the partial pressure of hydroiodic acid when the reaction has reached chemical equilibrium?

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
Initial (bar)	2.50		2.50		0
Change	-x		-x		+2x
Equil. (bar)	$2.50 - x$		$2.50 - x$		2x

$$59.3 = \frac{(2x)^2}{(2.50 - x)^2} \rightarrow \sqrt{59.3} = 7.7006 = \frac{2x}{2.50 - x} \rightarrow x = 1.9846 \text{ bar}$$

At Equil. (M)	0.515		0.515		3.97
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8. A mining engineer needs to separate lead from barium. To this end, they add  $\text{Na}_2\text{SO}_4$  slowly to a solution that is 0.1 M in  $\text{Pb}(\text{NO}_3)_2$  and 0.1 M in  $\text{Ba}(\text{NO}_3)_2$ . Which will precipitate first, Pb or Ba? Assume  $\text{Na}_2\text{SO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ , and  $\text{Ba}(\text{NO}_3)_2$  dissociate completely in solution.

$$(K_{\text{sp}} \text{PbSO}_4 = 1.8 \times 10^{-8}, K_{\text{sp}} \text{BaSO}_4 = 1.1 \times 10^{-10}).$$

**Because the Pb and Ba salts each dissociate in the same ratio (1:1) the  $K_{\text{sp}}$  values can be directly compared to determine which salt is more soluble. The salt with the lowest  $K_{\text{sp}}$  will precipitate first. For this reason,  $\text{BaSO}_4$  precipitates before  $\text{PbSO}_4$ .**

9. Calculate the solubility of  $\text{ZnCO}_3(\text{s})$  ( $K_{\text{sp}} \text{ZnCO}_3 = 3.0 \times 10^{-8}$ ) in:

- a) Pure water

	$\text{ZnCO}_3(\text{s})$	$\rightleftharpoons$	$\text{Zn}^{2+}(\text{aq})$	+	$\text{CO}_3^{2-}(\text{aq})$
[initial] M	-		0		0
[equil] M	-		x		x

$$3.0 \times 10^{-8} = x^2 \rightarrow x = 1.73 \times 10^{-4} \text{ M}$$

- b) 0.050 M  $\text{Zn}(\text{NO}_3)_2$ . Assume  $\text{Zn}(\text{NO}_3)_2$  dissociates completely in solution.

	$\text{ZnCO}_3(\text{s})$	$\rightleftharpoons$	$\text{Zn}^{2+}(\text{aq})$	+	$\text{CO}_3^{2-}(\text{aq})$
[initial] M	-		0.050		0
[equil] M	-		$0.050 + x$		x

$$3.0 \times 10^{-8} = (0.050 + x)x$$

$$\text{assume } x \text{ is small. } 3.0 \times 10^{-8} = (0.050)x \rightarrow x = 6.0 \times 10^{-7} \text{ M}$$

- c) Rationalize any differences in solubility between part a) and part b).

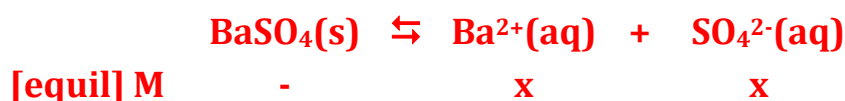
**The presence of  $\text{Zn}^{2+}$  (common ion from  $\text{ZnNO}_3$ ) decreases the solubility of  $\text{ZnCO}_3$  by approximately three orders of magnitude.**



10. **Good question.** Using the data in question 8, calculate the percentage of the first metal (Pb or Ba) that can be isolated as a precipitate before the second salt begins to precipitate.

**There are two methods to solve this problem, one approximate and one more accurate. Both are demonstrated below.**

**The solubility of BaSO<sub>4</sub> is:**



$$1.1 \times 10^{-10} = x^2 \rightarrow x = 1.05 \times 10^{-5} \text{ M}$$

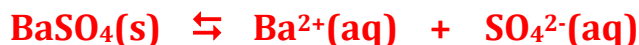
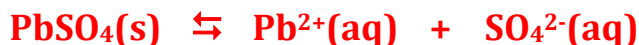
**This means at equilibrium [Ba<sup>2+</sup>(aq)] = 1.05 x 10<sup>-5</sup> M. The rest of the barium has to be precipitated as barium sulfate. Originally, 0.1M Ba(NO<sub>3</sub>)<sub>2</sub> dissociates completely in solution so the initial concentration of Ba<sup>2+</sup> was 0.1 M. As sulphate ion is added to the solution, it will precipitate the barium ion until the equilibrium concentration above is reached. This is an approximation because we are ignoring what the lead ions are doing. If we are not careful we might precipitate lead as sulphate is added. This effect is being ignored here.**

**Therefore, the amount that precipitated is**

$$\% \text{Ba}^{2+} \text{ precipitated} = \frac{(0.1 - 1.05 \times 10^{-5}) \text{ M}}{0.1 \text{ M}} \times 100\% = 99.99\%$$

**A more accurate method is to consider the PbSO<sub>4</sub> precipitate at the same time as BaSO<sub>4</sub>(s) so that both equilibria are treated together.**

**The two equilibria are:**



**Originally, 0.1M Pb(NO<sub>3</sub>)<sub>2</sub> dissociates completely in solution. Therefore, the initial concentration of Pb<sup>2+</sup> in solution is 0.1 M.**

**The Pb salt will begin to precipitate when [Pb<sup>2+</sup>][SO<sub>4</sub><sup>2-</sup>] > K<sub>sp</sub>.**

$$[\text{Pb}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}} \rightarrow 0.1\text{M}[\text{SO}_4^{2-}] = 1.8 \times 10^{-8} \rightarrow [\text{SO}_4^{2-}] = 1.8 \times 10^{-7}\text{M}$$

In a solution that is 0.1M in  $\text{Pb}^{2+}$ , the maximum concentration of  $\text{SO}_4^{2-}$  in solution before precipitation is  $1.8 \times 10^{-7}$  M. At higher concentrations of sulfate,  $\text{PbSO}_4$  will start to precipitate and we won't be able to purely isolate the first metal.

When the concentration of  $\text{SO}_4^{2-}$  is  $1.8 \times 10^{-7}$  M, the maximum concentration of barium at equilibrium is:

$$\begin{aligned} [\text{Ba}^{2+}][\text{SO}_4^{2-}] &= K_{\text{sp}} \rightarrow [\text{Ba}^{2+}][1.8 \times 10^{-7}] = 1.1 \times 10^{-10} \\ [\text{Ba}^{2+}] &= 6.11 \times 10^{-4}\text{M} \end{aligned}$$

So, with an initial concentration of  $\text{Ba}^{2+}$  at 0.1 M, we can increase the sulphate ion concentration up to  $1.8 \times 10^{-7}$  M without precipitating lead sulphate, and the concentration of barium ions at that sulphate concentration is  $6.11 \times 10^{-4}$  M.

Therefore, the amount of barium that precipitates up to that point is

$$\% \text{Ba}^{2+} \text{ precipitated} = \frac{(0.1 - 6.11 \times 10^{-4})\text{M}}{0.1\text{M}} \times 100\% = 99.39\%$$

As you can see, both methods give very similar results.

11. **Good Question.** Solution mining is used to procure magnesium chloride ( $K_{sp} = 738$ ) buried too deep for traditional mining methods. Holes are drilled into the ore so that water can be pumped through. The solid magnesium chloride then dissolves in the water, creating a brine mixture. This mixture is pumped back to the surface for processing.
- a) Consider a pump that can transfer a maximum of 1000 kg of brine to the surface in one cycle. Anything exceeding 1000 kg will cause the equipment to fail catastrophically. Your client wants each pump cycle to yield 352 kg of magnesium chloride. As an engineer working on this project, do you recommend this be done? Recall that the density of water is 1 kg/L.

**First determine the solubility of  $\text{MgCl}_2(\text{s})$  (at equilibrium)**

	$\text{MgCl}_2(\text{s})$	$\rightleftharpoons$	$\text{Mg}^{2+}(\text{aq})$	+	$2\text{Cl}^{-}(\text{aq})$
[initial] M	-		0		0
[equil.] M	-		x		2x

$$K_{sp} = [\text{Mg}^{2+}][\text{Cl}^{-}]^2 = (x)(2x)^2 \rightarrow x = 5.693\text{M}$$

**The solubility of  $\text{MgCl}_2(\text{s})$  is 5.693 M which gives the maximum amount of magnesium chloride the brine can hold. Use this number to determine the volume of brine needed to transport 352 kg of magnesium chloride, that is (molar mass  $\text{MgCl}_2 = 95.211 \text{ g/mol}$ )**

$$\text{Volume of brine} = \frac{\# \text{ moles } \text{MgCl}_2}{\text{solubility}} = \frac{\frac{352 \text{ kg}}{0.095211 \text{ kg mol}^{-1}}}{5.693\text{M}} = 649.4 \text{ L}$$

**Check if the solution exceeds 1000 kg. Here we make the approximation that the volume of water needed is the same as the volume of brine needed. (In reality, the volume will change when salt is dissolved in water but we need additional data to predict this, like the density of brine as a function of concentration).**

$$m_{\text{water}} + m_{\text{MgCl}_2} = (649.4 \text{ L}) \left( \frac{1\text{kg}}{1\text{L}} \right) + 352 \text{ kg} = 1001.4 \text{ kg}$$

**The mass just exceeds 1000 kg so the 352 kg yield is not recommended.**

- b) An alternate pump that can transfer 1000L of brine to the surface is used for the design. To cut costs, the idea of pumping process water instead of fresh water to dissolve the ore is proposed. The process water is recycled from elsewhere in the mine and has a concentration of 0.50 M  $\text{Mg}(\text{NO}_3)_2$ . How much “new” magnesium chloride can be brought up in one cycle? Is using process water a viable option?

	$\text{MgCl}_2(\text{s})$	$\rightleftharpoons$	$\text{Mg}^{2+}(\text{aq})$	+	$2\text{Cl}^{-}(\text{aq})$
[initial] M	-		0.50		0
[equilib]M	-		$0.50 + x$		$2x$

$$K_{sp} = [\text{Mg}^{2+}][\text{Cl}^{-}]^2 = (0.50 + x)(2x)^2$$

$$738 = (4x^2)(0.50 + x)$$

$$738 = 2x^2 + 4x^3$$

Put this into Wolfram Alpha

$$x = 5.531$$

So, the solubility of  $\text{MgCl}_2(\text{s})$  in the process water is 5.531 M. The maximum mass of magnesium chloride that can be procured in the process water cycle is:

$$5.531 \text{ M} \times 1000 \text{ L} \times \frac{95.211 \text{ g}}{\text{mol MgCl}_{2(\text{s})}} = 526612 \text{ g} = 526.6 \text{ kg}$$

while for the fresh water cycle it would be

$$5.693 \text{ M} \times 1000 \text{ L} \times \frac{95.211 \text{ g}}{\text{mol MgCl}_{2(\text{s})}} = 542036 \text{ g} = 542.0 \text{ kg}$$

The difference in magnesium chloride procured for fresh water and process water is small (15kg), so using process water is a viable option.