Thermodynamics

This worksheet should help you identify how we can use thermodynamics to understand chemical reactions and builds off the previous work in the unit. It is intended for you to work through it in order. *(Don't skip ahead.)*

Mercury chloride is an incredible toxic compound, where even a small exposure (<1 g) can kill a human in less than 24 hours. You are tasked with studying the dissolution of mercury chloride in water.

$$HgCl_{2\,(s)} \leftrightarrow \_\_\_ \, Hg^{2+}{}_{(aq)} + \underline{2} \, Cl^{-}{}_{(aq)}$$

	S° (J/mol K)	ΔH°f (kJ/mol)
$HgCl_{2\,(s)}$	146.0	-224.3
$Hg^{2+}{}_{(aq)}$	84.5	172.4
$Cl^{-}{}_{(aq)}$	56.5	-167.2

Use the table above to… Σ products - Σ reactants

Calculate the standard change in entropy for the reaction.

$\Delta S^\circ_{rxn} = (84.5\ J/mol \cdot K + 2(56.5\ J/mol \cdot K)) - (146.0\ J/mol \cdot K)$

$\Delta S^\circ_{rxn} = 197.5\ J/mol \cdot K - 146.0\ J/mol \cdot K$

$\Delta S^\circ_{rxn} = 51.5\ J/mol \cdot K$

Calculate the standard enthalpy of reaction.

$\Delta H^\circ_{rxn} = (172.4\ kJ/mol + 2(-167.2\ kJ/mol)) - (-224.3\ kJ/mol)$

$\Delta H^\circ_{rxn} = -162\ kJ/mol - {}^{-}224.3\ kJ/mol$

$\Delta H^\circ_{rxn} = 62.3\ kJ/mol$

Based on signs of enthalpy and entropy, do you expect the reaction to be spontaneous or nonspontaneous at standard conditions (25 °C)? Explain!

The ΔS°_{rxn} is (+) so the system is becoming more random. This is favorable.

The ΔH°_{rxn} is (+) so the reaction is endothermic. This is not favorable, energy needs to be added.

$\therefore$ unclear if spontaneous.

$\Delta S / 1000$

Calculate the standard free energy change of the reaction.

$$\Delta G^{\circ}_{rxn} = 62.3\ kJ/mol - 298\ K(0.0515\ kJ/mol \cdot K)$$

$$\Delta G^{\circ}_{rxn} = 46.9\ kJ/mol$$

nonspontaneous

How would you characterize the reaction? Reactants- or products-favored? Why?

Because the reaction is nonspontaneous it is reactants favored! It is not favored to move forward without external intervention.

Is the reaction always spontaneous or always nonspontaneous? Or is it dependent on temperature? If the reaction is dependent on temperature, when will the reaction be spontaneous?

ΔS $+$

ΔH $+$

The reaction will be spontaneous at high temp because the addition of energy will help with the endothermic process.

If you were to add excess solid $HgCl_2$ to water at room temp, the concentration of dissolved $HgCl_2$ would be 0.2752 M. How would you describe the solution? What IMF are present?

The solution would be saturated, as the question states excess solid was added and not all will dissolve. Because this is an ionic compound, ion-dipole will develop with H_2O. There will also be dispersion, dipole-dipole, & H bonding between water molecules.

How would the concentration change if you increased the temperature of the solution? Why?

We know that solubility of solids increases with increasing temp, so if temp is raised concentration should increase.

This also makes sense with our spontaniety calc... the reaction becomes spontaneous at high temp!

Determine the properties of 100.0 mL of the 0.2752 M $HgCl_2$ solution (assume a density of 1.03 g/mL). What is the vapor pressure, boiling point, and freezing point of the solution? The vapor pressure of pure water 25 ºC is 23.8 mmHg.

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$$\text{molality} = \frac{\text{moles solute}}{\text{Kg solvent}}$$

$$0.2752\ M = \frac{x}{0.100\ L} \qquad x = 0.02752 \text{ moles } HgCl_2$$

$$0.02752 \text{ moles } HgCl_2 \left| \frac{271.52\ g}{1\ \text{mole}} \right. = 7.472\ g \text{ solute}$$

$$100\ mL \left| \frac{1.03\ g}{1\ mL} \right. = 103\ g \text{ solution} - 7.472\ g \text{ solute} = 95.5\ g\ H_2O$$

$$\text{molality} = \frac{0.02752 \text{ moles}}{0.0955\ kg} = 0.288\ m$$

$HgCl_2$: $1 + 2 = 3$

$$\Delta BP = (3)(0.288\ m)(0.514\ °C/m)$$

$$\Delta BP = 0.444\ °C$$

$$T_{BP} = 100.44\ °C$$

$$\Delta FP = (3)(0.288\ m)(1.86\ °C/m)$$

$$\Delta FP = 1.61\ °C$$

$$T_{FP} = -1.61\ °C$$

If 25.0 mg is the threshold of toxicity for humans, what volume of the 0.2752 M solution would be enough to be lethal?

$$25{,}0\ mg \left| \frac{1\ g}{1000\ mg} \right| \frac{1\ mole}{271{,}52\ g} = 9.21\times10^{-5}\ moles$$

$$0{,}2752\ M = \frac{9.21\times10^{-5}\ moles}{x}$$

$$x = 0.000334\ L$$

$$\downarrow$$

$$0{,}33\ mL$$

$$P_{vap} = \chi_{H_2O} P^{\circ}_{vap}$$

$$\chi_{H_2O} = \frac{moles\ H_2O}{moles\ H_2O + moles\ HgCl_2 (3)}$$

$$95{,}9\ g\ H_2O \left| \frac{1\ mole\ H_2O}{18{,}01\ g\ H_2O} \right. = 5.325\ mole$$

$$\chi_{H_2O} = \frac{5.325\ moles}{5.325\ moles + 0.02752\ moles (3)}$$

$$= 0.9847$$

$$P_{vap} = (0{,}9847)(23.8\ mmHg)$$

$$= 23.4\ mmHg$$