

Spontaneous Processes

Which of the following processes are spontaneous?

(a) Separating a mixture of N_2 and O_2 into two separate samples

Non spontaneous

(b) Alignment of iron filings in a magnetic field

Spontaneous

(c) Dissolution of HCl(g) in water to form HCl(aq)

Spontaneous

(d) Sublimation of $\text{CO}_2(\text{s})$ at -100°C , 1 atm (CO_2 sublimation point is -78°C , 1 atm)

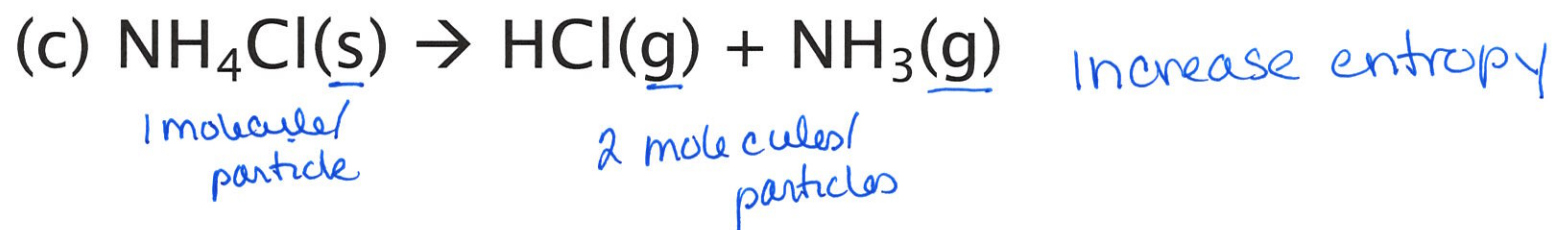
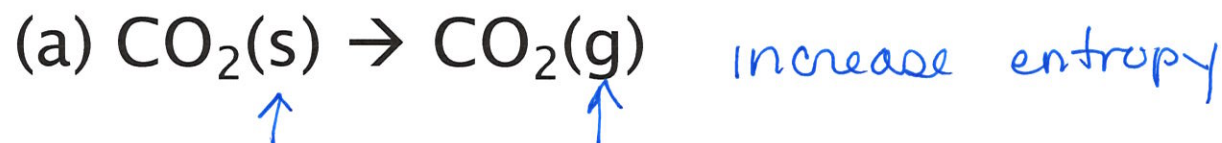
$-100^\circ\text{C} < -78^\circ\text{C}$ nonspontaneous

(e) Reaction of copper with oxygen to form CuO under typical environmental conditions in RI.

Spontaneous

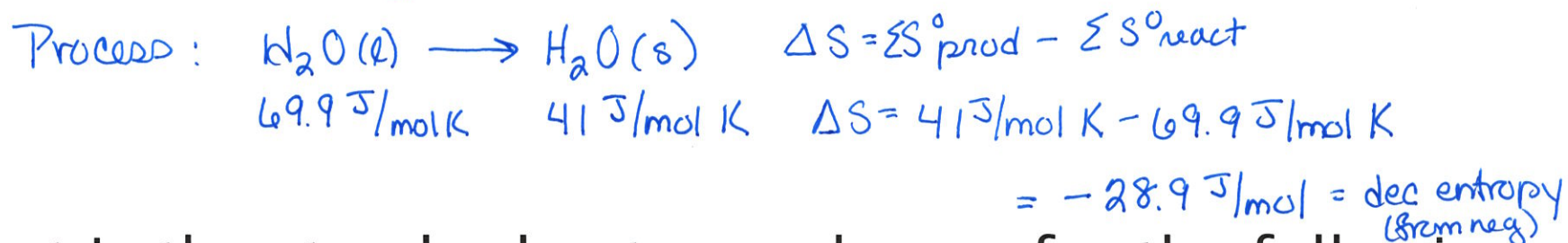
Predicting Entropy Changes

Indicate whether the following produces an increase or decrease in the entropy of the system:

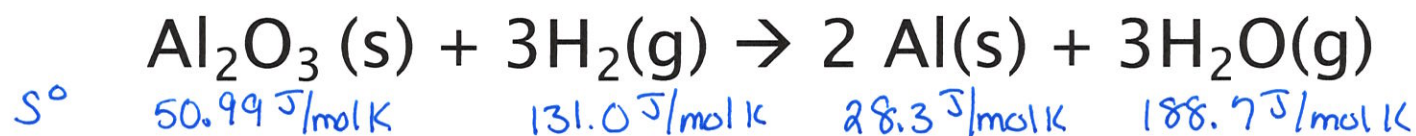


Calculating Reaction Entropy from Standard Entropies

1. What is the molar change in entropy for water freezing at 25°C? **A: -28.9 J/mol K**



2. What is the standard entropy change for the following reaction? **A: 178.7 J/mol K**



$$\Delta S = \sum S^\circ_{\text{prod}} - \sum S^\circ_{\text{react}}$$

$$\begin{aligned} \Delta S &= [2(28.3 \text{ J/mol K}) + 3(188.7 \text{ J/mol K})] - [1(50.99 \text{ J/mol K}) + 3(131.0 \text{ J/mol K})] \\ &= [56.6 \text{ J/mol K} + 566.1 \text{ J/mol K}] - [50.99 \text{ J/mol K} + 393.0 \text{ J/mol K}] \\ &= 622.7 \text{ J/mol K} - 443.99 \text{ J/mol K} = 178.71 \text{ J/mol K} \end{aligned}$$

$\rightarrow 178.7 \text{ J/mol K}$ increase entropy
entropically favored

Calculating Entropy (S) from ΔH

The normal boiling point of ethanol ($\text{C}_2\text{H}_5\text{OH}$, 46.07g/mol) is 78.3°C and its molar enthalpy of vaporization is 38.56 kJ/mol . What is the change in entropy in the system when 68.3g of gaseous ethanol at 1 atm condenses to liquid at the normal boiling point? **A: -163 J/K**

$$S = \frac{\Delta H}{T}$$

$$78.3^\circ\text{C} + 273.15 = 351.45\text{K}$$

↖ opposite process
sign of ΔH changes
 $\Delta H_{\text{cond}} = -38.56\text{ kJ/mol}$

$$68.3\text{g} \left(\frac{1\text{mol}}{46.07\text{g}} \right) = 1.4825\text{mol} \left(\frac{-38.56\text{ kJ}}{\text{mol}} \right) = -57.166\text{ kJ} = \Delta H$$

$$S = \frac{\Delta H}{T} = \frac{-57.166\text{ kJ}}{351.45\text{K}} = -0.163\text{ kJ/K} \times \frac{1000\text{ J}}{\text{kJ}} \\ = -163\text{ J/K}$$

Gibbs Free Energy & Spontaneity

1. A certain reaction has $\Delta H^\circ = -19.5 \text{ kJ}$ and $\Delta S^\circ = 42.7 \text{ J/K}$.

(a) Is the reaction exothermic or endothermic? **A: exothermic**

$$-\Delta H = \text{exothermic}$$

(b) Does the reaction lead to an increase or decrease in the randomness or disorder of the system? **A: increase**

entropy

+ $\Delta S = \text{increase entropy}$

(c) Calculate ΔG° at 298K **A: -32.2 kJ**

$$\Delta G = \Delta H - T \Delta S \quad 42.7 \text{ J/K} \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = 0.0427 \text{ kJ/K}$$

$$= -19.5 \text{ kJ} - 298 \text{ K} (0.0427 \text{ kJ/K})$$

$$= -19.5 \text{ kJ} - 12.746 \text{ kJ} = -32.246 \text{ kJ} \rightarrow \boxed{-32.2 \text{ kJ}}$$

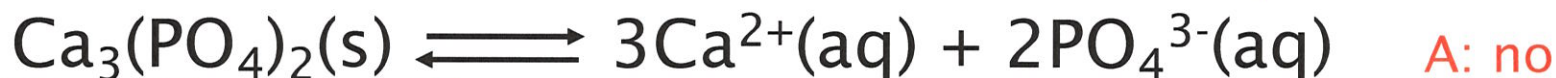
(d) Is the reaction spontaneous at 298K under standard conditions? **A: yes**

+ ΔG non spontaneous
- ΔG spontaneous

-32.2 kJ
neg $\Delta G = \text{is spontaneous}$

$-\Delta G$

2. Is the following process spontaneous at 25°C? at 75°C?



$$\Delta H^\circ = -4121 \text{ kJ/mol} \quad S^\circ = 236 \text{ J/mol K}$$

$$\Delta H^\circ = -542.96 \text{ kJ/mol}$$

$$\Delta H^\circ = -1277 \text{ kJ/mol}$$

Step 1: Calculate ΔH

$$S^\circ = -55.2 \text{ J/mol K}$$

$$S^\circ = -222 \text{ J/mol K}$$

$$\Delta H_{\text{rxn}} = \sum \Delta H_{\text{prod}} - \sum \Delta H_{\text{react}}$$

$$\Delta H_{\text{rxn}} = [3(-542.96 \text{ kJ/mol}) + 2(-1277 \text{ kJ/mol})] - [1(-4121 \text{ kJ/mol})]$$

$$= -1628.88 \text{ kJ/mol} + (-2554 \text{ kJ/mol}) - (-4121 \text{ kJ/mol})$$

$$= -4182.88 \text{ kJ/mol} + 4121 \text{ kJ/mol} = -61.88 \text{ kJ/mol}$$

Step 2: Calculate ΔS

$$\Delta S_{\text{rxn}} = \sum S^\circ_{\text{prod}} - \sum S^\circ_{\text{react}}$$

$$\Delta S_{\text{rxn}} = [3(-55.2 \text{ J/mol K}) + 2(-222 \text{ J/mol K})] - [1(236 \text{ J/mol K})]$$

$$= -165.6 \text{ J/mol K} - 444 \text{ J/mol K} - 236 \text{ J/mol K}$$

$$= -845.6 \text{ J/mol K} \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = -0.8456 \text{ kJ/mol K}$$

Step 3: Calculate ΔG $25^\circ\text{C} + 273.15 = 298.15 \text{ K}$ $75^\circ\text{C} + 273.15 = 348.15 \text{ K}$

@25°C $\Delta G = \Delta H - T\Delta S$

@75°C

$$\Delta G = -61.88 \text{ kJ/mol} - 298.15 \text{ K}(-0.8456 \text{ kJ/mol K})$$

$$= -61.88 \text{ kJ/mol} + 252.16 \text{ kJ/mol}$$

$$= +190.24 \text{ kJ/mol} \quad \text{not spontaneous}$$

$$\Delta G = -61.88 \text{ kJ/mol} - 348.15 \text{ K}(-0.8456 \text{ kJ/mol K})$$

$$= -61.88 \text{ kJ/mol} + 294.396 \text{ kJ/mol}$$

$$= +232.52 \text{ kJ/mol}$$

Even less spontaneous!

3. At what temperature will the following process become spontaneous?



From previous question:

$$\Delta H_{\text{rxn}} = -61.88 \text{ kJ/mol}$$

$$\Delta S_{\text{rxn}} = -0.8456 \text{ kJ/mol K}$$

+ ΔG nonspontaneous

- ΔG spontaneous

transition $\Delta G = 0$

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

$$0 \text{ kJ/mol} = -61.88 \text{ kJ/mol} - T(-0.8456 \text{ kJ/mol K})$$

$$+61.88 \text{ kJ/mol} \quad +61.88 \text{ kJ/mol}$$

$$\frac{61.88 \text{ kJ/mol}}{0.8456 \text{ kJ/mol K}} = \frac{(T)(0.8456 \text{ kJ/mol K})}{0.8456 \text{ kJ/mol K}}$$

$$T = 73.18 \text{ K} - 273.15 = -199.97^\circ\text{C}$$

A: -200°C

Free Energy & Equilibrium

1. Calculate ΔG° for the following reaction at 25°C.



K_{sp} for Fe(OH)_2 is 1.6×10^{-14}

A: 79 kJ/mol

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

$$\text{where } R = 8.314 \times 10^{-3} \text{ kJ/mol K}$$

$$T = \text{temp in K}$$

$$K = \text{equilibrium constant}$$

$$\Delta G = -(8.314 \times 10^{-3} \text{ kJ/mol K})(298.15 \text{ K})(\ln 1.6 \times 10^{-14})$$

$$\Delta G = (-2.4788)(-31.766) \text{ kJ/mol}$$

$$\Delta G = 78.742 \text{ kJ/mol} \rightarrow 78.7 \text{ kJ/mol}$$

$$\hookrightarrow 79 \text{ kJ/mol}$$

2. For the following reaction:



A: (a) -5.41 kJ/mol
(b) 0.295 kJ/mol

- (a) Using data from Appendix 2, calculate ΔG° at 298K
(b) Calculate ΔG at 298K if the partial pressure of NO_2 and N_2O_4 are 0.40atm and 1.60atm, respectively.

(a) $\text{NO}_2(\text{g}) \quad \Delta H_f^\circ = 33.85 \text{ kJ/mol}$
 $S^\circ = 240.46 \text{ J/mol K}$

$\text{N}_2\text{O}_4(\text{g}) \quad \Delta H_f^\circ = 9.66 \text{ kJ/mol}$
 $S^\circ = 304.3 \text{ J/mol K}$

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

$$\Delta H_{\text{rxn}} = 9.66 \text{ kJ/mol} - 2(33.85 \text{ kJ/mol})$$

$$9.66 \text{ kJ/mol} - 67.7 \text{ kJ/mol} = -58.04 \text{ kJ/mol}$$

$$\Delta S_{\text{rxn}} = 304.3 \text{ J/mol K} - 2(240.46 \text{ J/mol K}) =$$

$$304.3 \text{ J/mol K} - 480.92 \text{ J/mol K} = -176.62 \text{ J/mol K} \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = -0.17662 \text{ kJ/mol K}$$

$$\Delta G^\circ = -58.04 \text{ kJ/mol} - 298 \text{ K}(-0.17662 \text{ kJ/mol K})$$

$$-58.04 \text{ kJ/mol} + 52.63 \text{ kJ/mol} = \boxed{-5.41 \text{ kJ/mol}} = \Delta G^\circ$$

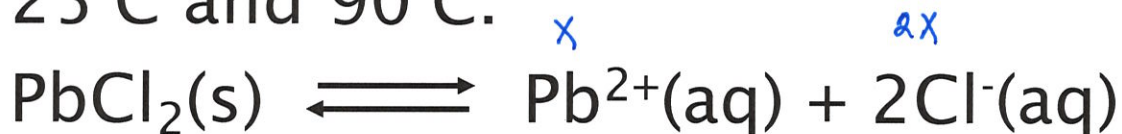
(b) $\Delta G = \Delta G^\circ + RT \ln Q = -5.41 \text{ kJ/mol} + (8.314 \times 10^{-3} \text{ kJ/mol K})(298 \text{ K})(\ln \left[\frac{1.60}{0.40^2} \right])$

$\ln(10) = 2.3026$

$$\Delta G = -5.41 \text{ kJ/mol} + 5.705 \text{ kJ/mol}$$

$$= \boxed{0.295 \text{ kJ/mol}}$$

3. Compare the molar solubility of lead chloride at 25°C and 90°C.



K_{sp} for PbCl_2 is 1.6×10^{-5} at 25°C

From Table:

ΔH_f° (kJ/mol)

S° (J/molK)

$\text{PbCl}_2(\text{s}) = -359$

$\text{PbCl}_2(\text{s}) = 136$

$\text{Pb}^{2+}(\text{aq}) = -1.7$

$\text{Pb}^{2+}(\text{aq}) = 10.5$

$\text{Cl}^{-}(\text{aq}) = -167.2$

$\text{Cl}^{-}(\text{aq}) = 56.5$

@ 25°C → regular molar solubility

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 = [x][2x]^2 = 1.6 \times 10^{-5}$$

$$90 + 273.15 = 363.15 \text{ K}$$

$$4x^3 = 1.6 \times 10^{-5} \quad x^3 = 4.0 \times 10^{-6}$$

$$x = 1.59 \times 10^{-2} \text{ M @ 25°C}$$

@ 90°C $\Delta G = -RT \ln K$ $\Delta G = \Delta H - T \Delta S$

$$\Delta H = [-1.7 \text{ kJ/mol} + 2(-167.2 \text{ kJ/mol})] - [-359 \text{ kJ/mol}] = 22.9 \text{ kJ/mol}$$

$$\Delta S = [10.5 \text{ J/molK} + 2(56.5 \text{ J/molK})] - 136 \text{ J/molK} = -12.5 \text{ J/molK} \rightarrow -0.0125 \text{ kJ/molK}$$

$$\Delta G = 22.9 \text{ kJ/mol} - (363.15 \text{ K})(-0.0125 \text{ kJ/molK})$$

$$22.9 \text{ kJ/mol} + 4.54 \text{ kJ/mol} = 27.44 \text{ kJ/mol}$$

$$\Delta G = -RT \ln K$$

$$27.44 \text{ kJ/mol} = (-8.314 \times 10^{-3} \text{ kJ/molK})(363.15 \text{ K})(\ln K)$$

$$\frac{27.44 \text{ kJ/mol}}{-3.02 \text{ kJ/mol}} = \frac{-3.02 \text{ kJ/mol} \times \ln K}{-3.02 \text{ kJ/mol}} \quad \ln K = -9.086$$

$$K = e^{-9.086} = 1.13 \times 10^{-4} = K_{\text{sp}} @ 90^\circ\text{C}$$

$$1.13 \times 10^{-4} = 4x^3 \quad \frac{3.05 \times 10^{-2} \text{ M}}{1.59 \times 10^{-2} \text{ M}} = 1.9$$

$$x^3 = 2.83 \times 10^{-5}$$

$$x = 3.05 \times 10^{-2} \text{ M @ 90°C}$$

A: solubility at 90°C about double the solubility at 25°C