

15.2 Entropy and spontaneity

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1. Which reaction has the greatest positive entropy change?

- a. $\text{CH}_4(\text{g}) + 1\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ 2.5 moles \rightarrow 3 moles (all gas)
~~b.~~ $\text{CH}_4(\text{g}) + 1\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ 2.5 moles \rightarrow 3 moles (\rightarrow l)
 c. $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ 3 moles \rightarrow 3 moles (all gas)
~~d.~~ $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ 3 moles \rightarrow 3 moles (\rightarrow l)

more simp

2. Some chlorine gas is placed in a flask of fixed volume at room temperature. Which change will cause a decrease in entropy?

- a. Adding a small amount of hydrogen
 b. Adding a small amount of chlorine
 c. Cooling the flask
 d. Exposing the flask to sunlight

increase # particles
 creating more order (g \rightarrow l)
 adding temp

3. Identify the process expected to have a value of ΔS closest to zero?

- a. $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$ 2 moles \rightarrow 1 mole
 b. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$ 2 moles \rightarrow 2 moles (all gas)
 c. $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ 1 mole \rightarrow 2 moles (s + g)
 d. $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ l \rightarrow g

4. Predict the entropy change ΔS for the following reactions.

- a. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ ΔS - 4 moles - 2 moles
 b. $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightarrow \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$ ΔS - more complex iron 7 moles \rightarrow 2 moles
 c. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(\text{s}) + 2\text{NH}_4\text{SCN}(\text{s}) \rightarrow \text{Ba}(\text{SCN})_2(\text{aq}) + 2\text{NH}_3(\text{aq}) + 10\text{H}_2\text{O}(\text{l})$
 ΔS 3 moles \rightarrow 13 moles s \rightarrow aq / l

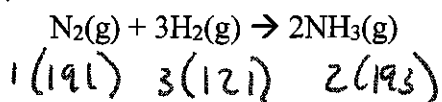
5. Which is the best description of the entropy and enthalpy changes accompanying the sublimations of iodine: $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$?

- a. $\Delta S+$, $\Delta H+$, reaction is endothermic
 b. $\Delta S+$, $\Delta H-$, reaction is exothermic
 c. $\Delta S-$, $\Delta H+$, reaction is endothermic
 d. $\Delta S-$, $\Delta H-$, reaction is exothermic

s \rightarrow g (4s), breaking IMF_s

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6. Calculate the entropy change ΔS for the Haber process shown from tabulated standard molar entropies at 25°C.



$$\begin{aligned} \Delta S_{\text{rxn}} &= \sum \Delta S_{\text{p}} - \sum \Delta S_{\text{r}} \\ &= 2(193) - [191 + 3(121)] \\ &= -198 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

7. Under what circumstances is a reaction spontaneous at all temperatures?

	ΔH^\ominus	ΔS^\ominus
A.	+	+
B.	+	-
C.	-	-
D.	-	+

want ΔG_-

$$\therefore -\Delta H - (+T\Delta S) = -\#$$

8. For the process: $C_6H_6(l) \rightarrow C_6H_6(s)$

The standard entropy and enthalpy changes are:

$$\Delta H^\ominus = -9.83 \text{ kJ mol}^{-1} \text{ and } \Delta S^\ominus = -35.2 \text{ J K mol}^{-1}.$$

a. Predict and explain the effect of an increase in temperature on the spontaneity of the process.

Since $\Delta S(-)$ + $\Delta G = \Delta H - T\Delta S$, larger T increase (+) value of $T\Delta S$, less spontaneous

b. $\Delta H^\ominus = -9.83 \text{ kJ mol}^{-1}$ and $\Delta S^\ominus = -35.2 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the temperature (in $^\circ\text{C}$) at which $\Delta G = 0$ for the above process and explain the significance of this temperature.

$$0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{-9.83}{-0.0352} = 279 \text{ K} \rightarrow \text{6}^\circ\text{C melting pt}$$

Point in which l & s are @ eqm

9. The ΔH^\ominus and ΔS^\ominus values for a certain reaction are both positive. Which statement is correct about the spontaneity of this reaction at different temperatures?

- It will be spontaneous at all temperatures.
- It will be spontaneous at high temperatures but not at low temperatures.
- It will be spontaneous at low temperatures but not at high temperatures.
- It will not be spontaneous at any temperature.

$$\Delta G = \Delta H \rightarrow, \text{ not}$$

$$\Delta G = -T\Delta S \text{ @ high temps, is (overcomes } \Delta H +)$$

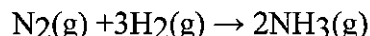
10. Explain in terms of ΔG^\ominus , why a reaction for which both ΔH^\ominus and ΔS^\ominus values are positive can sometimes be spontaneous and sometimes not.

$\Delta G(-)$ spontaneous, $\Delta G(+)$ non spontaneous

@ high temps, $\Delta G(-)$ due to $-T\Delta S > \Delta H$

@ low temps, $\Delta G(+)$ due to $-T\Delta S < \Delta H$

11. Consider the following reaction.



- (i) Use values from section 11 in the Data Booklet to calculate the enthalpy change, ΔH^\ominus , for this reaction.

$$\begin{aligned} & 1(\text{N}=\text{N})_2 + 6(\text{H}-\text{H}) \rightarrow 6(\text{N}-\text{H}) \\ & 1(+945) + 3(+436) + 6(-391) \\ & \quad -93 \text{ kJ mol}^{-1} \end{aligned}$$

- (ii) The magnitude of the entropy change, ΔS , at 27 °C for the reaction is $62.7 \text{ J K}^{-1} \text{ mol}^{-1}$. State, with a reason, the sign of ΔS .

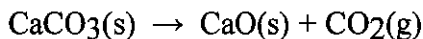
$$\Delta S (-), 4 \text{ moles (g)} \rightarrow 2 \text{ moles (g)}$$

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- (iii) Calculate ΔG for the reaction at 27 °C and determine whether this reaction is spontaneous at this temperature.

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &= (-93) - (300 \text{ K})(-0.0627) \\ &= -74.2 \text{ kJ mol}^{-1} \text{ (spontaneous)} \end{aligned}$$

12. The equation for the decomposition of calcium carbonate is given below.



At 500 K, ΔH for this reaction is $+177 \text{ kJ mol}^{-1}$ and ΔS is $161 \text{ J K}^{-1} \text{ mol}^{-1}$.

- (a) Explain why ΔH for the reaction above cannot be described as ΔH_f^\ominus .

cannot be \ominus = not under std conditions (Temp)

cannot be f = not forming from elements (decomposing)

- (b) State the meaning of the term ΔS .

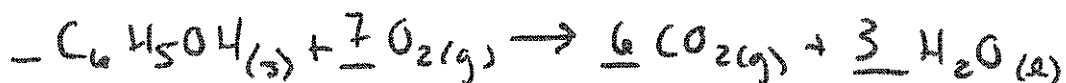
change in entropy \rightarrow degree of disorder

- (c) Calculate the value of ΔG at 500 K and determine, giving a reason, whether or not the reaction will be spontaneous

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= (+177) - (500)(+0.161) \\ &= 96.5 \text{ kJ mol}^{-1} \text{ (not spontaneous due to (+) value)}\end{aligned}$$

13. The standard enthalpy change for the combustion of phenol, $\text{C}_6\text{H}_5\text{OH}(\text{s})$, is $-3050 \text{ kJ mol}^{-1}$ at 298 K.

- (a) Write an equation for the complete combustion of phenol.



- (b) The standard enthalpy changes of formation of carbon dioxide, $\text{CO}_2(\text{g})$, and of water, $\text{H}_2\text{O}(\text{l})$, are -394 kJ mol^{-1} and -286 kJ mol^{-1} respectively.

Calculate the standard enthalpy change of formation of phenol, $\text{C}_6\text{H}_5\text{OH}(\text{s})$.

$$\begin{aligned}\Delta H_f &= \sum \Delta H_p - \sum \Delta H_r \\ -3050 &= [6(-394) + 3(-286)] - x \\ &= -172 \text{ kJ mol}^{-1}\end{aligned}$$

- (b) The standard entropy change of formation, ΔS^\ominus , of phenol, $\text{C}_6\text{H}_5\text{OH}(\text{s})$ at 298 K is $-385 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the standard free energy change of formation, ΔG^\ominus , of phenol at 298 K.

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= (-172) - (298)(-0.385) \\ &= -57.3 \text{ kJ mol}^{-1}\end{aligned}$$

- (c) Determine whether the reaction is spontaneous at 298 K, and give a reason.

Spontaneous $\Delta G(-)$

- (e) Predict the effect, if any, of an increase in temperature on the spontaneity of this reaction.

Become less spontaneous, ΔG becomes more (+)
due to $\Delta S(-)$