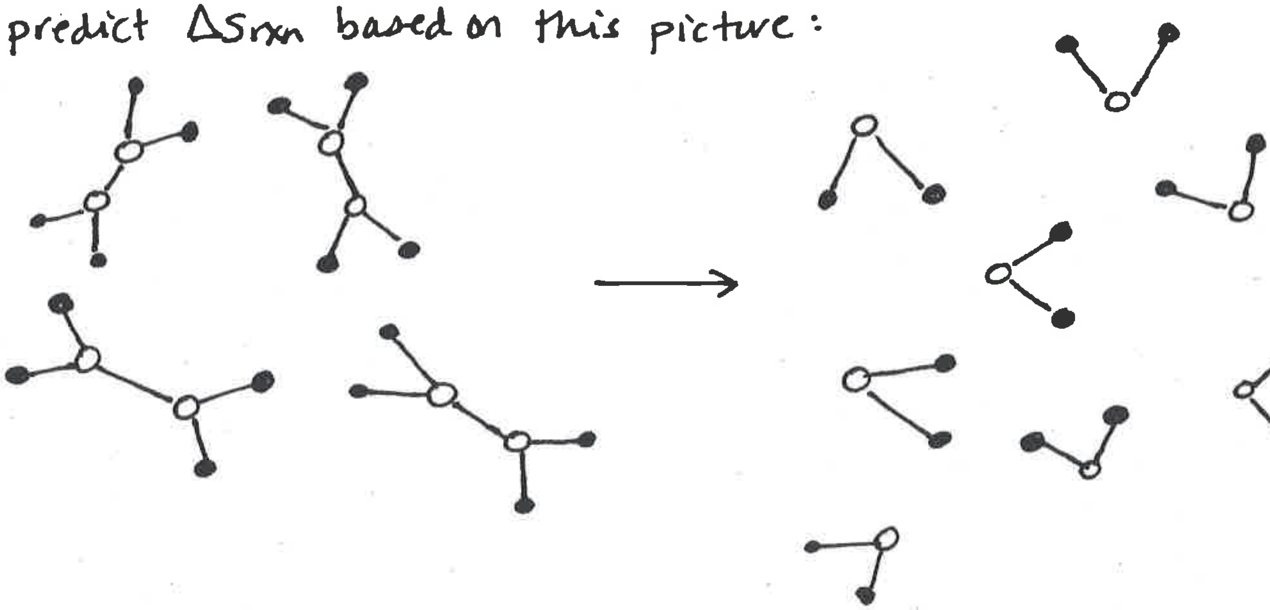
Chapter 19

④ predict ΔS_{rxn} based on this picture:



ΔS_{rxn} is <u>positive</u>.

Reactants and products both appear to be gas phase since the molecules are randomly oriented, and a bit too far apart to be liquid phase (though close for a gas..)
as the number of gas molecules increases, entropy increases, since the number of ways in which to organize/partition the energy increases. (Δn_{gas} = ⊕ so ΔS_{rxn} = ⊕)

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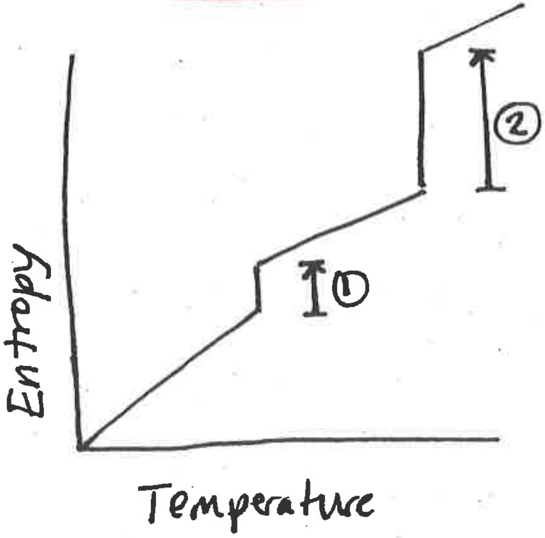
⑤



a) ① corresponds to melting; the entropy change is ΔS_{fusion}

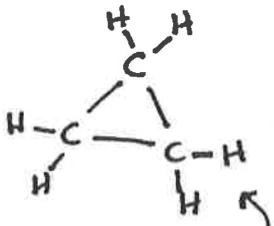
② represents vaporization; the entropy change is ΔS_{vap}

b) $\Delta S_{vaporization}$ is generally larger than ΔS_{fusion} because there is more of increase in ways to distribute energy / more of an increase in the number of microstates (W) when vaporizing than in melting.

for example, when melting, the solid transitions from a substance with an essentially perfect crystal structure to a substance (liquid) that still has many molecules oriented in <u>specific</u> directions, due to polarity or geometry. but in vaporization, all of the intermolecular attractions are overcome (since the molecules separate further away), so the molecules can be randomly organized/oriented/spaced, so <u>many</u> more microstates become available.
Also, the volume increase is <u>much</u> more significant in vaporization than in melting. Entropy increases as V increases, since more possible ways to partition energy increase.

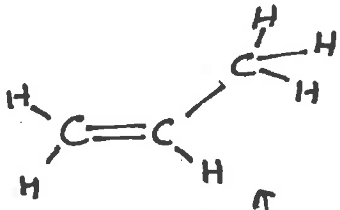
Chapter 19

(48) Which isomer of C_3H_6 would have <u>higher molar entropy</u> at 25°C?



cyclopropane

or



propene

propene has more entropy; it has more ways in which to distrubute rotational and vibrational energy. Though propene's π bond can't rotate, its sigma bonds can, so the right carbon can rotate, however individual atoms in the cyclopropane are not free to rotate since the ring would break... Also, propene has 3 types of bonds: C=C, C–C, C–H (and the C-H bonds aren't really even identical in strength), and cyclopropane has only two types: C–C, C–H. so propene has more ways to distribute vibrational energy.

(53) Use Appendix C to calculate ΔS°_{rxn} and explain the sign of ΔS.

$$\Delta S_{rxn} = \sum S_f(\text{products}) - \sum S_f(\text{reactants})$$

(a) $\underset{219.4}{C_2H_{4(g)}} + \underset{130.58}{H_{2(g)}} \rightarrow \underset{229.5}{C_2H_{6(g)}}$

negative since the number of gas molecules decreases. $\Delta n_{gas} = -1$

$(229.5) - (219.4) - (130.58) = -120.48 \rightarrow \boxed{-120.5\ J/K}$

(b) $\underset{304.3}{N_2O_{4(g)}} \rightarrow \underset{240.5}{2\ NO_{2(g)}}$

positive since the number of gas molecules increases.

$2(240.5) - (304.3) = \boxed{176.7\ J/Kelvin}$

$\Delta n_{gas} = 2 - 1 = 1$

$\Delta n_{gas} = +1$

(c) $\underset{50.21}{Be(OH)_{2(s)}} \longrightarrow \underset{13.77}{BeO_{(s)}} + \underset{188.83}{H_2O_{(g)}}$

positive since the number of gas molecules increases.

$(13.77) + (188.83) - (50.21) = \boxed{152.39\ J/K}$ $\Delta n_{gas} = 1 - 0 = +1$

(d) $\underset{237.6}{2\ CH_3OH_{(g)}} + \underset{205.0}{3\ O_{2(g)}} \longrightarrow \underset{213.6}{2\ CO_{2(g)}} + \underset{188.83}{4\ H_2O_{(g)}}$

$2(213.6) + 4(188.83) - 2(237.6) - 3(205.0) = 92.32 \rightarrow \boxed{92.3\ J/K}$

positive since the number of gas molecules increases! $\Delta n_{gas} = 6 - 5 = +1$

$\boxed{\textbf{19.59}}$ Use the given information to calculate ΔG° for each reaction, and then classify each reaction as spontaneous or nonspontaneous at 25°C.

(c) $2\,PCl_{3(g)} + O_{2(g)} \text{ -----> } 2\,POCl_{3(g)}$ $\Delta H^\circ rxn = -508.3$ kJ/mole $\Delta S^\circ rxn = -178.4$ J/K-mole

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -508.3\,\frac{kJ}{mole} - (298.15\,K)\left(-0.1784\,\frac{kJ}{mole}\right)$$

$$= \boxed{-455.1\ kJ/mole}$$ Spontaneous (since ΔG° is ⊖)

(d) $2\,CH_3OH_{(g)} + H_{2(g)} \text{ -----> } C_2H_{6(g)} + 2\,H_2O_{(g)}$

ΔG°formation (kJ/mole) : -161.9 0 -32.89 -228.6

$$\Delta G^\circ_{rxn} = \Sigma\Delta G_f^\circ(\text{products} - \Sigma\Delta G_f^\circ(\text{reactants}))$$ spontaneous

$$= (-32.89) + 2(-228.6) - 2(-161.9) - 1(0) = -166.29 \rightarrow \boxed{-166.3\ \frac{kJ}{mole}}$$

$\boxed{\textbf{19.61}}$ For parts (a) and (b), use the given information to calculate ΔG° for each reaction.

(a) $2\,SO_{2(g)} + O_{2(g)} \text{ -----> } 2\,SO_{3(g)}$ $\Delta H^\circ rxn = -196.6$ kJ/mole $\Delta S^\circ rxn = -189.6$ J/K-mole

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = \left(-196.6\,\frac{kJ}{mole}\right) - (298.15\,K)(-0.1896\ kJ/mole\cdot K)$$

$$= -140.07 \rightarrow \boxed{-140.1\ kJ/mole}$$ (a)

(b) $NO_{2(g)} + N_2O_{(g)} \text{ -----> } 3\,NO_{(g)}$

ΔG°formation (kJ/mole) : 51.84 103.59 86.71

$$\Delta G^\circ_{rxn} = \Sigma\Delta G_f^\circ(\text{prod.}) - \Sigma\Delta G_f^\circ(\text{reactants})$$

$$= 3(86.71) - 1(51.84) - 1(103.59) = \boxed{104.70\ kJ/mole}$$ (b)

(c) Calculate Kp (Keq) for the reaction in (a) at 25°C, and classify the rxn as spontaneous or nonspontaneous at 25°C.

$\Delta G^\circ =$ ⊖ and $K > 1$ so $\boxed{\text{spontaneous}}$

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

$$K = e^{-\Delta G^\circ/RT} = e^{\left(\frac{+140.07\ kJ/mole}{(.008314\ \frac{kJ}{mol\cdot K})(298.15\,K)}\right)} = e^{56.51} = \boxed{3.47\times10^{24}}$$ (c)

(d) Calculate Kp (Keq) for the reaction in (b) at 25°C, and classify the rxn as spontaneous or nonspontaneous at 25°C.

$$K = e^{-\Delta G^\circ/RT} = e^{\frac{-104.70}{.008314\cdot 298.15}} = e^{-42.238} = \boxed{4.53\times10^{-19}}$$

$\boxed{\text{not spontaneous}}$ since $\Delta G =$ ⊕ and $Keq < 1$

(19.61 continued)

(e) Use the Keq to calculate ΔG° for this reaction, and classify the rxn as spontaneous or nonspontaneous at 25°C.

$HC_2H_3O_2$ <--------> $H^{+1}_{(aq)} + C_2H_3O_2^{-1}{}_{(aq)}$ Keq = 1.8×10^{-5}.

$K_{eq} < 1$ and $\Delta G^\circ = \oplus$

so $\boxed{\text{not spontaneous}}$

$$\Delta G^\circ = -RT \ln K = -\left(8.314 \frac{J}{mol\cdot K}\right)(298.15\,K)\ln(1.8\times10^{-5})$$

(e)

$$= 27081\ J/mol \quad \boxed{27000\ \frac{J}{mol}} \text{ or } \boxed{27\ \frac{kJ}{mol}}$$

(f) Use the Keq to calculate ΔG° for this reaction, and classify the rxn as spontaneous or nonspontaneous at 25°C.

$H^{+1}_{(aq)} + NO_2^{-1}{}_{(aq}$ <--------> $HNO_{2(aq)}$ Keq = 2200

$\boxed{\text{Spontaneous}}$

$$\Delta G^\circ = -RT \ln K = -\left(8.314 \frac{J}{mol\cdot K}\right)(298.15K)\ln(2200)$$

(f)

$$= -19078 \rightarrow \boxed{-19000\ \frac{J}{mole}} \text{ or } \boxed{-19\ \frac{kJ}{mole}}$$

19.65 Classify each of the following reactions as one of the four possible types summarized in Table 19.3:) (for what types of temperatures will it be spontaneous?)

(a) $N_2(g) + 3F_2(g) \longrightarrow 2NF_3(g)$
$\Delta H^\circ = -249$ kJ; $\Delta S^\circ = -278$ J/K

$$\Delta G^\circ = \underset{\ominus}{\Delta H^\circ} - T\underset{\ominus}{\Delta S^\circ}$$

ΔG° will be negative at low temp and positive at high temp,

$\boxed{\text{so spontaneous at low T, not spont at high T}}$ (a)

(b) $N_2(g) + 3Cl_2(g) \longrightarrow 2NCl_3(g)$
$\Delta H^\circ = 460$ kJ; $\Delta S^\circ = -275$ J/K

$$\Delta G^\circ = \underset{\oplus}{\Delta H^\circ} - T\underset{\ominus}{\Delta S^\circ}$$

ΔG° will be positive for all temp, so

$\boxed{\text{not spontaneous at any temperature}}$ (b)

(c) $N_2F_4(g) \longrightarrow 2NF_2(g)$
$\Delta H^\circ = 85$ kJ; $\Delta S^\circ = 198$ J/K

$$\Delta G^\circ = \underset{\oplus}{\Delta H^\circ} - T\underset{\oplus}{\Delta S^\circ}$$

ΔG° will be positive at low T and negative for high T

$\boxed{\text{is spontaneous at high T is not spontaneous at low T.}}$ (c)

Table 19.3:

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
−	+	−	−	Spontaneous at all temperatures	$2O_3(g) \longrightarrow 3O_2(g)$
+	−	+	+	Nonspontaneous at all temperatures	$3O_2(g) \longrightarrow 2O_3(g)$
−	−	+	+ or −	Spontaneous at low T; nonspontaneous at high T	$H_2O(l) \longrightarrow H_2O(s)$
+	+	−	+ or −	Spontaneous at high T; nonspontaneous at low T	$H_2O(s) \longrightarrow H_2O(l)$

Chapter 19

(67) A reaction is spontaneous at 390 K.

$\Delta H_{rxn} = +23.7$ kJ

What can you conclude about the sign and magnitude of ΔS_{rxn}?

If the rxn is spontaneous at 390 K,

$\boxed{\Delta S_{rxn} \text{ must be positive.}}$

ΔH is positive (rxn is endothermic), and this alone would lead to a nonspontaneous/unfavorable rxn. So the only way to make the rxn favorable is to have a favorable (positive) ΔS_{rxn}.

$\boxed{\begin{array}{l} T\Delta S \text{ must be larger than } \Delta H \\ \text{or } \Delta S \text{ must be larger than } \Delta H/T \end{array}}$

we could solve for the minimum positive value of ΔS since we know rxn is spont. at 390 K

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0$$

$$23.7\text{ kJ} - (390\text{ K})\Delta S^\circ < 0$$

$$\Delta S^\circ > .061\text{ kJ/mol}\cdot\text{K}$$

$$\Delta S^\circ > 61\text{ J/mol}\cdot\text{K}$$

ΔS must be at least this large.

Since the rxn is endothermic, it absorbs heat energy from its surroundings, reducing the entropy of its surroundings.

In order to make the overall $\Delta S_{universe}$ positive ($\Delta S_{universe} = \Delta S_{rxn} + \Delta S_{surroundings}$), the ΔS_{rxn} must be a large enough positive number to compensate for the negative $\Delta S_{surroundings}$.

19.83 Consider the decomposition of Barium Carbonate:

$$BaCO_{3(s)} \text{ -----> } BaO_{(s)} + CO_{2(g)}$$

	$BaCO_{3(s)}$	$BaO_{(s)}$	$CO_{2(g)}$
ΔH°f (kJ/mole) :	-1216.3	-553.5	-393.5
S°f (J/mole-Kelvin) :	112.1	70.4	213.6

a. Calculate ΔH°rxn and ΔS°rxn.

ΔH°rxn: $(-553.5) + (-393.5) - (-1216.3) = \boxed{269.3 \text{ KJ/mole}}$

ΔS°rxn: $(70.4) + (213.6) - (112.1) = \boxed{171.9 \text{ J/mol}\cdot\text{K}}$

b. Calculate Kp for the rxn at 25°C.

$$\Delta G^o = \Delta H^o - T\Delta S^o = (269.3) - (298.15\text{ K})(0.1719 \tfrac{\text{KJ}}{\text{mol}\cdot\text{K}}) = 218.048 \tfrac{\text{KJ}}{\text{mol}}$$

$$K_p = e^{-\Delta G^o/RT} = e^{\frac{-218048\text{ J/mol}}{8.314\frac{\text{J}}{\text{mol}\cdot\text{K}}\cdot 298.15\text{K}}} = e^{-87.96} = \boxed{6.27 \times 10^{-39}} \quad (b)$$

c. Write an expression for Kp in terms of the appropriate substances. $\boxed{K_p = P_{CO_2}}$ (c)

d. Calculate Kp at 1100 K

First calculate ΔG° at 1100 K, assuming that ΔH° and ΔS° are indepndat of temp.

$$\Delta G^o = \Delta H^o - T\Delta S^o = (269.3 \text{ KJ/mole}) - (1100\text{ K})(0.1719 \text{ KJ/mol}\cdot\text{K}) = 80.21 \text{ KJ/mole}$$

then calculate K_p

$$K_p = e^{-\Delta G^o/RT} = e^{\frac{-80.21 \text{ KJ/mole}}{(.008314\frac{\text{KJ}}{\text{mol}\cdot\text{K}})(1100\text{K})}} = e^{-8.771} = \boxed{0.00016 \text{ or } 1.6\times 10^{-4}} \quad (d)$$

e. Calculate the temperature range for which the reaction is spontaneous
(that is, for what set of temperatures is Kp > 1?)

(again, assuming constant ΔH and ΔS)

$$\Delta G^o = \Delta H^o - T\Delta S^o = 0$$
$$269.3 - T(0.1719) = 0$$
$$T = 1566\text{ K}$$

$\boxed{T > 1566\text{ K or } T > 1293\,^\circ\text{C to be spontaneous}}$

f. Explain why this reaction would be expected to be more favorable at high/low temperature (which one?) based on the sign of ΔH and/or ΔS rxn.

ΔH is positive (endothermic)

endothermic rxns are more favorable at high T than at low T.

Chapter 19

(73) Use Data in App. C to estimate boiling pt of C_6H_6 (benzene)

$$\boxed{C_6H_{6(l)} \longrightarrow C_6H_{6(g)}}$$

ΔH_f°	49.0	82.9	kJ/mole
S_f°	172.8	269.2	J/mol·K

$\Delta H_{vaporization}$ = 82.9 − 49.0 = $\underline{33.9}$ kJ/mole

ΔS_{vap} = (269.2 − 172.8) J/K·mole = $\underline{96.4}$ J/K·mole

To find the boiling point, we need to find the temperature at which the vapor pressure of benzene is 1.00 atm

$$K_p = p_{C_6H_6} = 1$$

In other words, we need to find the temp at which

$K_{eq} = 1$ and $\Delta G^\circ = 0$ (the temp above which rxn becomes "spontaneous")

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$33.9 \frac{kJ}{mole} - T(.0964 \frac{kJ}{mol \cdot K}) = 0$$

$$T = \frac{33.9 \text{ kJ/mole}}{.0964 \text{ kJ/K mole}} = 351.7 \text{ K} \text{ or } 78.5\text{ °C}$$

3SF

(a) $\boxed{79\text{ °C}}$

(b) Acc to wikipedia and our textbook, the actual boiling point of  is 80.1 °C. Why is there a difference?

The ΔH_{vap} and ΔS_{vap} values we used were reported at 25 °C. These values can change slightly as temperature changes - they are <u>slightly</u> dependent on temperature. We assumed that they were independent of temperature, so our value is slightly different from the book (experimental) value.

(90) $2\,Mg_{(s)} + O_{2(g)} \rightarrow 2\,MgO_{(s)}$

Second Law of Thermo says that in any spontaneous process, entropy of the universe must increase. yet, this rxn has a negative value for ΔS ($\Delta n_{gas} = -1$) and is still spontaneous. Is this inconsistent?

Nope! $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

$$\Delta S_{universe} = \Delta S_{rxn} - \frac{\Delta H_{rxn}}{T}$$

ΔS_{rxn} is negative, so this alone would decrease the entropy of the universe. However, this rxn is highly exothermic! ($\Delta H_{rxn} = 2 \cdot \Delta H_f(MgO) = -1203.6\,kJ$)

so the " $-\frac{\Delta H_{rxn}}{T}$ " term will be positive, and will be larger than $|\Delta S_{rxn}|$, so the overall $\Delta S_{universe}$ will increase.

In other words, when the rxn releases heat energy into its surroundings, this added energy (from the surroundings perspective) will cause surroundings to increase entropy. The increase in entropy in the surroundings more than compensates for the decrease in entropy in the system/rxn.