

Lecture 25

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

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

Question #2, p. 25

Consider the process: $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$

for which, $\Delta H_{\text{fusion}} = 6.03 \text{ kJ/mol}$ and $\Delta S_{\text{fusion}} = 22.1 \text{ J/K mol}$. Calculate ΔG at -10°C , 0°C , and 10°C ?

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At -10°C (263 K):

$$\Delta G = \Delta H - T\Delta S = 6030 \text{ J} - (263 \text{ K}) 22.1 \text{ J/K}$$

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$$\Delta G = \Delta H - T\Delta S = 6030 \text{ J} - (263 \text{ K}) 22.1 \text{ J/K}$$

$$\Delta G = 6030 \text{ J} - 5810 \text{ J} = 220 \text{ J}$$

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$$\Delta G = \Delta H - T\Delta S = 6030 \text{ J} - (263 \text{ K}) 22.1 \text{ J/K}$$

$$\Delta G = 6030 \text{ J} - 5810 \text{ J} = 220 \text{ J} \quad (\text{positive } \Delta G)$$

As expected, this process is not spontaneous at -10°C (ice doesn't melt at -10°C).

Using $\Delta G = \Delta H - T\Delta S$
Question #2, p. 25 (cont)

At 10°C:

$$\Delta G = \Delta H - T\Delta S = 6030 \text{ J} - 283 \text{ K} (22.1 \text{ J/K})$$

Using $\Delta G = \Delta H - T\Delta S$
Question #2, p. 25 (cont)

At 10°C:

$$\Delta G = \Delta H - T\Delta S = 6030 \text{ J} - 283 \text{ K} (22.1 \text{ J/K})$$

$$\Delta G = 6030 - 6250 = -220 \text{ J (spontaneous)}$$

Using $\Delta G = \Delta H - T\Delta S$
Question #2, p. 25 (cont)

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Yes, ice melts at 10°C.

Using $\Delta G = \Delta H - T\Delta S$
Question #2, p. 25 (cont)

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Yes, ice melts at 10°C.

At 0°C:

$$\Delta G = \Delta H - T\Delta S = 6030 \text{ J} - 273 \text{ K} (22.1 \text{ J/K})$$

Using $\Delta G = \Delta H - T\Delta S$
Question #2, p. 25 (cont)

At 10°C:

$$\Delta G = 6030 \text{ J} - 283 \text{ K} (22.1 \text{ J/K})$$

$$\Delta G = 6030 - 6250 = -220 \text{ J (spontaneous)}$$

Yes, ice melts at 10°C.

At 0°C:

$$\Delta G = \Delta H - T\Delta S = 6030 \text{ J} - 273 \text{ K} (22.1 \text{ J/K})$$

$$\Delta G = 6030 - 6030 = 0 \text{ (at equilibrium)}$$

Results of the Calculation of ΔS_{univ} and ΔG°
for the Process $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ at -10°C , 0°C , and 10°C

Table 17.4 ► Results of the Calculation of ΔS_{univ} and ΔG° for the Process $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ at -10°C , 0°C , and 10°C *

T ($^\circ\text{C}$)	T (K)	ΔH° (J/mol)	ΔS° (J/K · mol)	$\Delta S_{\text{surr}} = -\frac{\Delta H^\circ}{T}$ (J/K · mol)	$\Delta S_{\text{univ}} = \Delta S^\circ + \Delta S_{\text{surr}}$ (J/K · mol)	$T\Delta S^\circ$ (J/mol)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (J/mol)
-10	263	6.03×10^3	22.1	-22.9	-0.8	5.81×10^3	$+2.2 \times 10^2$
0	273	6.03×10^3	22.1	-22.1	0	6.03×10^3	0
10	283	6.03×10^3	22.1	-21.3	+0.8	6.25×10^3	-2.2×10^2

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

Consider the process: $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$

for which, $\Delta H_{\text{fusion}} = 6.03 \text{ kJ/mol}$ and $\Delta S_{\text{fusion}} = 22.1 \text{ J/K mol}$.

+ +

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

Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependence of Spontaneity on Temperature

Table 17.5 ▶ Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependence of Spontaneity on Temperature

Case	Result
ΔS positive, ΔH negative	Spontaneous at all temperatures
ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
ΔS negative, ΔH negative	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	Process not spontaneous at <i>any</i> temperature (reverse process is spontaneous at <i>all</i> temperatures)

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$$\begin{array}{c} + \quad + \\ \Delta G = \Delta H - T\Delta S \end{array}$$

Note that this process is spontaneous above some temperature (at $T > 0^\circ\text{C}$). Whenever ΔH and ΔS are both positive, the reaction will be spontaneous (ΔG negative) when the favorable ΔS term dominates. This occurs at high temperatures (at temps above some value).

Lecture Question

Which reaction on p. 24 of the Handouts book is only spontaneous below some temperature (is only spontaneous at low temperatures)?

- a. Reaction 1
- b. Reaction 2
- c. Reaction 3
- d. Reaction 4

Lecture Question

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

Which reaction on p. 24 of the Handouts book is only spontaneous below some temperature (is only spontaneous at low temperatures)?

a. Reaction 1

b. Reaction 2; this reaction has negative values for both ΔH and for ΔS . At low temps the favorable ΔH term dominates and the rxn is spontaneous.

c. Reaction 3

d. Reaction 4

Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependence of Spontaneity on Temperature

Table 17.5 ▶ Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependence of Spontaneity on Temperature

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

Question #3, p.25

Given that: $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$ has $\Delta H_{\text{vap}} = 31.0$ kJ/mol and $\Delta S_{\text{vap}} = 93.0$ J/K mol, calculate the boiling point for bromine.

Question #3, p.25

Given that: $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$ has $\Delta H_{\text{vap}} = 31.0$ kJ/mol and $\Delta S_{\text{vap}} = 93.0$ J/K mol, calculate the boiling point for bromine.

At the boiling point, we are at equilibrium so $\Delta G = 0$.

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

Question #3, p.25

Given that: $\text{Br}_2(l) \rightarrow \text{Br}_2(g)$ has $\Delta H_{\text{vap}} = 31.0$ kJ/mol and $\Delta S_{\text{vap}} = 93.0$ J/K mol, calculate the boiling point for bromine.

At the boiling point, we are at equilibrium so $\Delta G = 0$.

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

For Br_2 :

$$T_{\text{bp}} = \frac{\Delta H}{\Delta S} = \frac{31,000 \text{ J}}{93.0 \text{ J/K}} = 333 \text{ K} = \text{boiling point}$$

Lecture Question

(Based on Question 4, p.25)

Consider the reaction:

$2 \text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) \rightarrow 3 \text{S}(\text{s}) + 2 \text{H}_2\text{O}(\text{g})$ along with the data in question 4, p. 25. How many of the following statements are true?

- I. This reaction is not spontaneous at standard conditions.
 - II. This reaction is endothermic.
 - III. This reaction will be spontaneous at very high temperatures.
- a. 0 (none) b. 1 c. 2 d. 3 (All statements are true.)

Lecture Question

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

Consider the reaction:

$2 \text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) \rightarrow 3 \text{S}(\text{s}) + 2 \text{H}_2\text{O}(\text{g})$ along with the data in question 4, p. 25. How many of the following statements are true?

- I. This reaction is not spontaneous at standard conditions. **Because ΔG° is negative ($\Delta G^\circ = -90. \text{ kJ}$), this reaction is spontaneous at standard conditions.**
 - II. This reaction is endothermic. **Reaction is exothermic.**
 - III. This reaction will be spontaneous at very high temperatures. **When ΔH and ΔS are both negative, the reaction is spontaneous below some temperature.**
- a. 0 (none) b. 1 c. 2 d. 3 (All statements are true.)