Supplemental Questions
for
Thermodynamics 2

1a. Calculate ΔG^0 for the reaction C (s, diamond) → C (s, graphite) from the thermodynamic information given below.

Species	ΔH_f^0 (kJ/mole)	S^0 ($J{\cdot}K^{-1}{\cdot}mole^{-1}$)	ΔG_f^0 (kJ/mole)
C (s, graphite)	0	5.740	0
C (s, diamond)	+1.895	2.377	+2.900

$$\Delta G^0 = \Delta G_f^0\ (C, s, graphite) - \Delta G_f^0\ (C, s, diamond)$$

$$\Delta G^0 = 0.000 - +2.900\ kJ/mole = -2.900\ kJ/mole$$

This reaction has a ΔG^0 of -2.900 kJ/mole.

b. Is this reaction spontaneous at 298.15K?

The reaction is spontaneous as written at 298.15K, because ΔG^0 (defined at 298.15K) is negative.

c. What is ΔS^0 for the reaction C (s, diamond) → C (s, graphite)? What does this ΔS^0 imply about any differences between diamond's and graphite's structures?

$$\Delta S^0 = S^0\ (C, s, graphite) - S^0\ (C, s, diamond)$$

$$\Delta S^0 = 5.740 - 2.377\ J{\cdot}K^{-1}{\cdot}mole^{-1} = +3.363\ J{\cdot}K^{-1}{\cdot}mole^{-1}$$

This reaction has a ΔS^0 of +3.363 $J{\cdot}K^{-1}{\cdot}mole^{-1}$. The positive ΔS implies that on going from diamond to graphite there are more ways in which to arrange the C atoms, which means that graphite's structure is less ordered in some way relative to diamond's structure.

d. Ignoring the temperature dependence of S and H, predict the temperature at which the reaction C (s, graphite) → C (s, diamond) becomes spontaneous.

This reaction becomes spontaneous at a temperature where $\Delta G^0 = 0$. So starting with the equation $\Delta G = \Delta H - T\Delta S$, we can write

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

$$\Delta H = T\Delta S$$

We don't know ΔH for this reaction, so we first need to determine it.

$$\Delta H^0 = \Delta H_f^0 \text{ (C, s, diamond)} - \Delta H_f^0 \text{ (C, s, graphite)}$$

$$\Delta H^0 = +1.895 \text{ kJ/mole} - 0.000 \text{ kJ/mole} = +1.895 \text{ kJ/mole}$$

For the conversion of graphite to diamond, ΔS^0 has the opposite sign of ΔS^0 for the conversion of diamond to graphite. Therefore, ΔS^0 is -3.363 $J \cdot K^{-1} \cdot mole^{-1}$.

Solving $\Delta H = T\Delta S$ for T and substituting in gives

$$T = \frac{\Delta H}{\Delta S} = \frac{+1.895x10^3 J \cdot mole^{-1}}{-3.363 J \cdot K^{-1} \cdot mole^{-1}} = -563.5K$$

This reaction is predicted to become spontaneous at -563.5 K. This a physically unreasonable answer because absolute temperature is never negative. We must, therefore, conclude that this reaction never becomes spontaneous.

2a. From the given thermodynamic data, calculate the temperature, in Kelvin, at which the reaction H_2O (l) → H_2O (g) becomes spontaneous.

Species	ΔH_f^0 (kJ/mole)	S^0 (J/K·mole)	ΔG_f^0 (kJ/mole)
H_2O (l)	-285.830	69.91	-237.129
H_2O (g)	-241.818	188.825	-228.572

The reaction for boiling water is H_2O (l) → H_2O (g). ΔH^0 for this reaction can be written as

$$\Delta H^0 = \Delta H_f^0(H_2O, g) - \Delta H_f^0(H_2O, l) = -241.818 - (-285.830) \text{ kJ}$$
$$\Delta H^0 = +44.012 \text{ kJ}$$

and ΔS^0 is

$$\Delta S^0 = S^0(H_2O, g) - S(H_2O, l) = 188.825 - 69.91 \text{ J/K}$$
$$\Delta S^0 = +118.91_5 \text{ J/K} = +0.11891_5 \text{ kJ/K}$$

When this reaction becomes spontaneous $\Delta G^0 = 0$, so

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$
$$0 = \Delta H^0 - T\Delta S^0$$
$$T = \Delta H^0/\Delta S^0 = +44.012 \text{ kJ}/(+0.11891_5 \text{ kJ/K}) = 370.11 \text{ K}$$

The boiling of water becomes spontaneous at 370.11 K.

b. Why isn't your answer to part a 373.15 K?

There are two reasons. First, both *H* and *S* depend on temperature, and so Δ*H* and Δ*S* do also. We did not account for this in our calculation. The second reason has to do with definitions. The normal boiling point of water is 373.15 K (100.00 °C), which is measured at 1 atm of pressure. The ΔH_f^0 and S^0 are calculated under standard conditions of 1 bar. Because the pressures are not the same, there may be a small difference in the boiling point due to the difference in the pressure.

3. PbO can exist in a yellow or a red phase (recall a phases are forms of a substance that differ only in their arrangement of atoms, or ions, in space). The standard thermodynamic parameters for the two phases are shown in the table below.

	ΔH_f^0 kJ·mol^{-1}	ΔG_f^0 kJ·mol^{-1}	S^0 J·K^{-1}·mol^{-1}
PbO (s, yellow)	-217.32	-187.89	68.70
PbO (s, red)	-218.99	-188.93	66.50

a. Calculate ΔG^0 for the conversion of yellow PbO to red PbO. Which phase is more stable under standard conditions?

Start with the balanced chemical equation

PbO (s, yellow) → PbO (s, red)

The Gibbs energy change for this reaction is

$\Delta G^0 = \Delta G_f^0 \text{ (PbO, s, red)} - \Delta G_f^0 \text{ (PbO, s, yellow)}$

$\Delta G^0 = -188.93 \text{ kJ} - -187.89 \text{ kJ}$

$\Delta G^0 = -1.04 \text{ kJ}$

Because the phase change from yellow PbO to red PbO is spontaneous (ΔG^0 for the reaction PbO, yellow to PbO, red is negative), red PbO is more stable under standard conditions.

b. What does the difference in S^0 for the two forms of PbO tell you about any differences in solid state structure between the two forms?

The higher S^0 for yellow PbO indicates that its structure in more disordered in some way relative to that of red PbO.

4a. Below the boiling point, the change of state from liquid to gas is non-spontaneous. At the boiling point the change of state becomes spontaneous. Starting from $\Delta G = \Delta H - T\Delta S$, prove Trouton's Rule ($\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$), which relates ΔS for vaporization to ΔH for vaporization and the boiling point, T (in Kelvin).

At the boiling point the change of state from liquid to gas changes from being non-spontaneous to spontaneous, so $\Delta G = 0$

Beginning with the relationship for ΔG_{vap} in terms of ΔH_{vap} and ΔS_{vap},

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$$

Substituting in $\Delta G_{vap} = 0$ gives,

$$0 = \Delta H_{vap} - T\Delta S_{vap}$$

Solving for ΔS_{vap} gives

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$$

b. Hydrogen sulfide, H_2S, boils at -60.4°C and has a ΔS_{vap} of $+87.9\ J{\cdot}K^{-1}{\cdot}mole^{-1}$, while water has a ΔS_{vap} of $+109.1\ J{\cdot}K^{-1}{\cdot}mole^{-1}$ at its boiling point. From these data calculate ΔH_{vap} for each compound using Trouton's rule.

For H_2S

$$\Delta H_{vap} = T\Delta S_{vap} = (-60.4 + 273.15K)(+87.9J \cdot K^{-1} \cdot mole^{-1}) = +18.7kJ \cdot mole^{-1}$$

For H_2O

$$\Delta H_{vap} = T\Delta S_{vap} = (373.15K)(+109.1J \cdot K^{-1} \cdot mole^{-1}) = +40.71kJ \cdot mole^{-1}$$

ΔH_{vap} for H_2S is +18.7 kJ/mole and ΔH_{vap} for H_2O is +40.71 kJ/mole.

c. Both S and O are in the same group of the periodic table, but ΔS_{vap} and ΔH_{vap} are very different for H_2S and H_2O. What does this imply about the molecules in the liquid state?

> *Enthalpy changes reflect the strength of the interactions that hold particles together (either within a particle or between particles), while entropy changes reflect differences in how energy is distributed between the particles or how ordered the particles are.*
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> **The difference in ΔH_{vap} implies that the strength of the interaction between water molecules in the liquid state must be larger than that which holds H_2S molecules together, because it takes more energy (in the form of heat) to make H_2O boil than it does H_2S. We know that it must be the interaction between particles because boiling is a physical process (the substance undergoing the change does not change its composition) and not a chemical process, which would break the molecules apart.**
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> **The different ΔS_{vap} tells us that the way that the particles arrange themselves in H_2O is different than the way that they arrange themselves in H_2S. The higher ΔS_{vap} for H_2O also tells us that the arrangement of water molecules in the liquid state is somehow more ordered than the arrangement of H_2S molecules is.**