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Thermochemistry: conceptual questions

1. Determine if the following sentences are true or not, giving the reasons.

a) All exothermic reactions are spontaneous at any temperature

b) All exothermic reactions are spontaneous between 0 K and $T=\Delta H^0/\Delta S^0$

c) In a spontaneous reaction the change in entropy can be negative

d) In this change of phase, the change in entropy will be positive: $H_2O\ (l) \rightarrow H_2O\ (g)$

2. We have two standard enthalpies of formation of water: -285.5 kJ/mol and –242.5 kJ/mol. Determine

a) Which one corresponds to the enthalpy of liquid water and which to the enthalpy of vapor

b) The enthalpy change of condensation of water

3. In a reaction the changes of enthalpy and entropy are $\Delta H^0 > 0$ and $\Delta S^0 < 0$

Study the spontaneity of this process

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Thermochemistry: conceptual questions

4. Consider the combustion enthalpies of carbon, hydrogen and methanol. Do the following:

a) Write the balanced equations for each combustion reaction

b) Indicate which reactants and products have a 0 value in formation enthalpy change

c) Determine how to calculate the values of combustion enthalpies starting from formation enthalpies

d) Determine how to calculate the enthalpy of formation of methanol starting from combustion enthalpies

5. Given the following thermochemical equations

$$2\,H_2O_2\,(l) \rightarrow 2\,H_2O\,(l) + O_2\,(g) \qquad \Delta H = -196\ kJ$$

$$N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g) \qquad \Delta H = -92.4\ kJ$$

a) Determine the possible sign of changes in entropy in each of both chemical reactions

b) Determine the enthalpy change of decomposition per mole of ammonia

c) Discuss the spontaneity of both reactions

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1. Determine if the following sentences are true or not, giving the reasons.

a) All exothermic reactions are spontaneous at any temperature

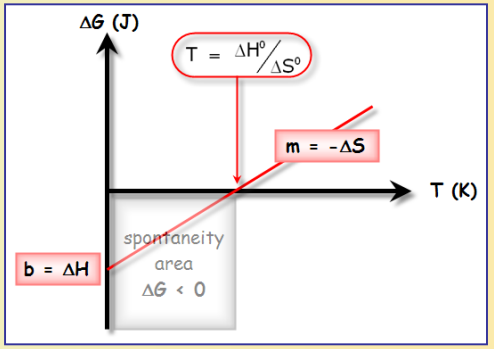
No, not always. At T=0 the reaction will be spontaneous, but at greater than 0 K temperatures, the entropy change plays a role that must be taken into account.

b) All exothermic reactions are spontaneous between 0 K and $T=\Delta H^0/\Delta S^0$

True. Exothermic reactions are spontaneous at T=0 K and the change in tendency (to nonspontaneous) happens when

$$\Delta G = \Delta H^0 - T * \Delta S^0 = 0 \rightarrow \Delta H^0 = T * \Delta S^0$$

$$T = \Delta H^0 / \Delta S^0$$



c) In a spontaneous reaction the change in entropy can be negative

Yes can be. In that case the reaction has to be exothermic (enthalpy change negative)

d) In this change of phase, the change in entropy will be positive: H_2O (l) $\rightarrow$ H_2O (g)

Yes, it will. The matter gains disorder (entropy) when liquid changes to a gas phase.

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2. We have two standard enthalpies of formation of water: -285.5 kJ/mol and –242.5 kJ/mol. Determine

a) Which one corresponds to the enthalpy of liquid water and which to the enthalpy of vapor

The lowest value (-285.5 kJ/mol) has to correspond to the formation of water in liquid phase.

b) The enthalpy change of condensation of water

From the enthapies we know, we can calculate that enthalpy of condensation:

$$H_2\,(g) + 0.5\,O_2\,(g) \rightarrow H_2O\,(l) \quad \Delta H = -285.5\ kJ$$

$$H_2O\,(g) \rightarrow H_2\,(g) + 0.5\,O_2\,(g) \quad \Delta H = +242.5\ kJ$$

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$$H_2O\,(g) \rightarrow H_2O\,(l) \quad \Delta H = -43\ kJ/mol$$

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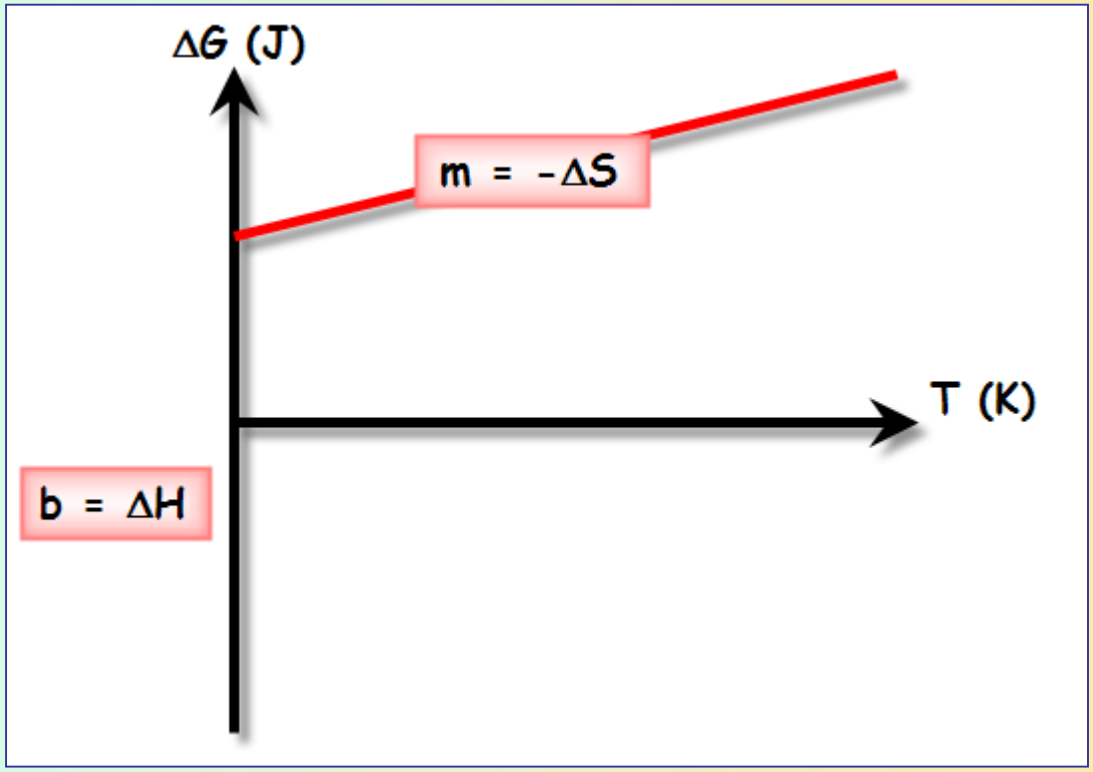
3. In a reaction the changes of enthalpy and entropy are $\Delta H^0 > 0$ and $\Delta S^0 < 0$

Study the spontaneity of this process

The process wil never be spontaneous. Graphically, it starts from a positive value ($\Delta H^0 > 0$) and the slope is positive (slope = $- \Delta S^0$). Therefore, ΔG will be always positive (that is, nonspontaneous)



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4. Consider the combustion enthalpies of carbon, hydrogen and methanol. Do the following:

a) Write the balanced equations for each combustion reaction

The balanced equations are:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$$

$$H_2\,(g) + 0.5\,O_2\,(g) \rightarrow H_2O\,(l)$$

$$CH_3OH\,(l) + 1.5\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l)$$

b) Indicate which reactants and products have a 0 value in formation enthalpy change

Only the enthalpies of formation of elements are zero:carbon, hydrogen and oxygen.

c) Determine how to calculate the values of combustion enthalpies starting from formation enthalpies

-The enthalpy of combustion of carbon is the same as the enthalpy of formation of carbon dioxide.

-The enthalpy of combustion of hydrogen is the same as the enthalpy of formation of water (liquid)

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4. Consider the combustion enthalpies of carbon, hydrogen and methanol. Do the following:

c) Determine how to calculate the values of combustion enthalpies starting from formation enthalpies

-The combustion enthalpy of methanol, from formation enthalpies:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_f\,[CO_2\,(g)]$$

$$H_2\,(g) + 0.5\,O_2\,(g) \rightarrow H_2O\,(l) \qquad \Delta H_f\,[H_2O\,(l)]$$

$$C\,(s) + 2\,H_2\,(g) + 0.5\,O_2\,(g) \rightarrow CH_3OH\,(l) \qquad \Delta H_f\,[CH_3OH\,(l)]$$

- - - -

$$CH_3OH\,(l) + 1.5\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l)$$

$$\Delta H_c\,[CH_3OH\,(l)] = \Delta H_f\,[CO_2\,(g)] + 2 * \Delta H_f\,[H_2O\,(l)] - \Delta H_f\,[CH_3OH\,(l)]$$

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4. Consider the combustion enthalpies of carbon, hydrogen and methanol. Do the following:

d) Determine how to calculate the enthalpy of formation of methanol starting from combustion enthalpies

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_c\,[C\,(s)]$$

$$H_2\,(g) + 0.5\,O_2\,(g) \rightarrow H_2O\,(l) \qquad \Delta H_c\,[H_2(g)]$$

$$CH_3OH\,(l) + 1.5\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l) \qquad \Delta H_c\,[CH_3OH\,(l)]$$

- - - -

$$C\,(s) + 2\,H_2\,(g) + 0.5\,O_2\,(g) \rightarrow CH_3OH\,(l) \qquad \Delta H_f\,[CH_3OH\,(l)]$$

$$\Delta H_f\,[CH_3OH\,(l)] = \Delta H_c\,[C\,(s)] + 2 * \Delta H_c\,[H_2\,(g)] - \Delta H_c\,[CH_3OH\,(l)]$$

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5. Given the following thermochemical equations

$$2\,H_2O_2\,(l) \rightarrow 2\,H_2O\,(l) + O_2\,(g) \quad \Delta H = -196\ kJ$$

$$N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g) \quad \Delta H = -92.4\ kJ$$

a) Determine the possible sign of changes in entropy in each of both chemical reactions

The change in entropy will be positive in the first case (a gas is produced) and negative in the second case (disorder –entropy- is lost)

b) Determine the enthalpy change of decomposition per mole of ammonia

$$NH_3\,(g) \rightarrow 0.5\,N_2\,(g) + 1.5\,H_2\,(g) \quad \Delta H = +\,46.2\ kJ/mol$$

c) Discuss the spontaneity of both reactions

-1st case: enthalpy chage is negative and entropy change is positive: the process will be always spontaneous

-2nd case: enthalpy change is negative and the entropy change is negative: the process will be spontaneous from T = 0 K to a given temperature.