

13.E: Spontaneous Processes (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed [here](#).

Q3

Write detailed calculation down for each question involved in gambling.

- How many "microstates" are there for the cards that come up from five random cards each from a separate deck?
- What is the probability of getting 5 queens of hearts?
- What is the probability of getting any specific hand of five cards?

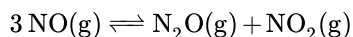
Solution

Microstates are specific configurations in which each particle is distinguishable. The number of ways that they can be arranged to describe the macrostate is the weight of that macrostate and used in the definition of entropy.

- The number of possible outcomes (microstates) of any repeated independent situation is equal to the number of possibilities in one iteration to the power of the repetitions. So in this case, the answer is 52 to the power of 5.
- One of these 52^5 possibilities.
- One of these 52^5 possibilities.

Q5

Is the above reaction spontaneous under 1 atm and room temperature? If so, what are the driving factors?



Solution

From a superficial overview of the reaction, we would conclude that the enthalpy change would be negative (i.e., $\Delta H < 0$) (why? more bonding in the products than the reactants). We would also expect a negative value of entropy ($\Delta n_{gas} < 0$). It is difficult to argue which would win from just looking at the reaction and we need to do a Hess's law like approach to solve numerically using the Gibbs energies of formation from [Table T1](#):

$$\Delta^\circ G_{rxn} = \Delta^\circ G_f\{\text{N}_2\text{O}\} + \Delta^\circ G_f\{\text{NO}_2\} - 3\Delta^\circ G_f\{\text{NO}\}$$

Q9

For each of the following scenarios predict the system's entropy change whether it is $\Delta S < 0$, $\Delta S = 0$, or $\Delta S > 0$.

- Increasing the amount of quarters being flipped from 2 to 4.
- Moving a child from a 30 ft. \times 30 ft. room to a 5 ft. \times 5 ft. room to play in.
- Increasing the temperature of a non-ideal polyatomic gas.

Solution

- Increasing the amount of flipped quarters leads to ($\Delta S > 0$) because it increases the number of microstates available. For example: $2^2 = 4$ so 4 microstates possible with 2 quarters but $2^4 = 16$ so 16 microstates are available with four quarters. $16 > 4$ so entropy would increase.
- If you divided the room in 1 sq. ft cubes as the places where the child may stand/play, there are only 25 squares in which the child could stand so 25 microstates versus 900 squares/microstates in the other room. Therefore $\Delta S < 0$ because there are less microstates available.
- Increasing the temperature of a non-ideal gas would lead to ($\Delta S > 0$) because the increased temperature would "unfreeze" "frozen" modes in the gas, which would allow it more degrees of freedom and therefore microstates.

Q10

Determine whether the change in entropy for the processes listed down below are positive or negative:

- condensing of iodine gas into a solid

b. diffusion of an ideal gas

Solution

- Change in entropy is negative, as gaseous iodine turns solid, the decreased freedom of movement restricts the possible particle locations and hence there is a decrease in the number of microstates.
- Change of entropy is positive. As diffusion occurs, there is increased freedom of movement and increase in the possible particle locations and an increase in the number of microstates.

Q11

Osmium melts at 3,027 °C and has an enthalpy change of fusion of 31.0 kJ/mol. Calculate the entropy of fusion of osmium.

Solution

Define the system at 1 mole of solid osmium at its melting point of 3027°C (3300 K). Imagine adding 31.0 kJ of heat infinitely slowly in such a way that the temperature remains constant, as the osmium melts. The heat is then equal to the q_{rev} for the melting. Substitute the value of heat supplied and T into the equation that defines the entropy of the change of the entropy of a system. Because the change occurs at a constant temperature, T may be outside the integral sign

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int dq_{\text{rev}} = \frac{1}{T} q_{\text{rev}} = \frac{31.0 \times 10^3 \text{ J mol}^{-1}}{3300 \text{ K}} = 9.39 \text{ J K}^{-1} \text{ mol}^{-1}$$

Tip. The temperature must be an absolute temperature (in Kelvins, for example).

Q13

Trouton's Rule is used to estimate the molar enthalpy of vaporization. What is iodine's enthalpy of vaporization if its normal boiling point is 184.4°C?

Solution

Trouton's Rule:

$$\Delta H_{\text{vap}} = \Delta S_{\text{vap}} T_b \quad (13.E.1)$$

$$\Delta S_{\text{vap}} \approx 88 \frac{\text{J}}{\text{K mol}} \quad (13.E.2)$$

$$T_b = 184.4^\circ \text{C} = 457.55 \text{ K} \quad (13.E.3)$$

$$\Delta H_{\text{vap}} = \left(88 \frac{\text{J}}{\text{K mol}} \right) (457.55 \text{ K}) = 40264.4 \frac{\text{J}}{\text{mol}} = 40.26 \frac{\text{kJ}}{\text{mol}} \quad (13.E.4)$$

Enthalpy of vaporization of iodine is 40.26 kJ/mol

Q15

If 0.250 mol Argon is expanded reversibly and isothermally at 400 K in its compressible oven from an initial volume of 12.0 L to a final volume of 30.0 L, what will the ΔU , q , w , ΔH , and ΔS for the gas?

Solution

For an isothermal process, $\Delta U = 0$, and consequently, $\Delta H = 0$. However, for the work:

$$w = \int_{v_o}^{v_f} P dV$$

Where:

$$P = \frac{nRT}{V}$$

meaning that if we put P into terms of V using $PV=nRT$, then we can get the work, which comes out look like:

$$w = nRT \ln \frac{V_f}{V_o}$$

$$w = (0.250 \text{ mol}) \times (8.314 \frac{\text{J}}{\text{Kmol}}) \times (400 \text{ K}) \times \ln \frac{30.0 \text{ L}}{12.0 \text{ L}} = 761.8 \text{ J}$$

$PV = nRT$ is the ideal gas law. it implies that the molecules or atoms of the gas are point masses, they have no volume and undergo only elastic collision.

Therefore, by the first law, the heat, q , must be the negative of the work. Now, as for ΔS , we know:

$$\Delta S = \frac{-q}{T}$$

which implies that:

$$\Delta S = nR \ln \frac{V_f}{V_o}$$

$$\Delta S = (0.250 \text{ mol}) \times (8.314 \frac{\text{J}}{\text{Kmol}}) \times \ln \frac{30.0 \text{ L}}{12.0 \text{ L}} = 1.90 \frac{\text{J}}{\text{K}}$$

Q17

Consider this. Exactly 2 moles of ice undergoes three different processes.

- I. heated reversibly at atmospheric pressure from temperature X to 0°C , then
- II. melted reversibly at 0°C . Finally
- III. it was heated reversibly at atmospheric pressure up to an unknown temperature Y .

Find temperature X & Y and identify ΔS_{sur} .

Given:

- $\Delta H_{\text{fus}} = 6007 \text{ J.mol}^{-1}$
- $C_p(\text{ice}) = 38 \text{ J.K}^{-1}.\text{mol}^{-1}$
- $C_p(\text{water}) = 75 \text{ J.K}^{-1}.\text{mol}^{-1}$
- $\Delta S_{\text{I}} = 12.034 \text{ J.K}^{-1}$
- $\Delta S_{\text{III}} = 136 \text{ J.K}^{-1}$

Solution

Since entropy changes are additive (thanks for them being state functions) and we have the entropy changes for Step I and Step III, all we need to do is calculate ΔS_{II} . However, we need to calculate temperatures first.

The equation below can be used to calculate ΔS_{sys} for a temperature change.

$$\Delta S = nC_p \ln \left(\frac{T_2}{T_1} \right) \quad (13.E.5)$$

To solve for unknown temperature, the equation can be arranged in this way.

$$\exp\left(\frac{\Delta S}{nC_p}\right) = \frac{T_2}{T_1} \quad (13.E.6)$$

Assuming the C_p stays constant throughout all the temperature change. Initial temperature X and final temperature Y can be found using the formula below.

$$T_x = T_2 \left(\exp\left(\frac{\Delta S_{\text{I}}}{nC_p}\right) \right)^{-1} = (273.15 \text{ K}) \left(\exp\left(\frac{12.034 \text{ J.K}^{-1}}{(2.00 \text{ mol})(38 \text{ J.K}^{-1}.\text{mol}^{-1})}\right) \right)^{-1} = 233.15 \text{ K} \quad (13.E.7)$$

$$T_y = T_1 \left(\exp\left(\frac{\Delta S_{\text{III}}}{nC_p}\right) \right) = (273.15 \text{ K}) \left(\exp\left(\frac{136 \text{ J.K}^{-1}}{(2.00 \text{ mol})(75 \text{ J.K}^{-1}.\text{mol}^{-1})}\right) \right) = 298.15 \text{ K} \quad (13.E.8)$$

ΔS_{II} must also be determined to obtain the ΔS_{system} .

Since the temperature remains constant in the second step, $\Delta S = q_{rev}$.

$$\Delta S_{II} = 2 \text{ mol} \times \frac{6007 \text{ J/mol}}{273.15 \text{ K}} = 43.984 \text{ J} \cdot \text{K}^{-1} \quad (13.E.9)$$

Since the entire process is reversible,

$$\Delta S_{surr} + \Delta S_{system} = 0$$

so

$$\Delta S_{surr} = -\Delta S_{system}.$$

Now we add the three entropy changes:

$$-\Delta S_{system} = -(\Delta S_I + \Delta S_{II} + \Delta S_{III}) \quad (13.E.10)$$

$$= -(12.034 + 43.984 + 136) \text{ J} \cdot \text{K}^{-1} \quad (13.E.11)$$

$$= -80.15 \text{ J} \cdot \text{K}^{-1} \quad (13.E.12)$$

$$= \Delta S_{surr} \quad (13.E.13)$$

Q18

Suppose 2 moles of water at standard temperature (25°C) and pressure is spontaneously evaporated by allowing it to fall onto a nickel plate maintained at 125°C. Calculate ΔS for the water, ΔS for the nickel plate, and ΔS_{total} if $C_{p(H_2O)(l)} = 75.4 \text{ J/(K.mol)}$ and $C_{p(H_2O)(g)} = 36.0 \text{ J/(K.mol)}$. Take $\Delta H_{vap} = 40.68 \text{ KJ/mol}$ for water and its boiling point of 100°C.

Solution

$$q_1 = \Delta H = mc\Delta T = 2 \times 75.4 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (100 - 25) = 11310 \text{ J} \quad (13.E.14)$$

$$q_2 = 40680 \frac{\text{J}}{\text{mol}} \times 2 = 81.36 \times 10^3 \text{ J} \quad (13.E.15)$$

$$q_3 = \Delta H = mc\Delta T = 2 \times 36 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (125 - 100) = 1800 \text{ J} \quad (13.E.16)$$

$$q_{total} = 11310 + 81.36 \times 10^3 + 1800 = 94470 \text{ J} \quad (13.E.17)$$

$$\Delta S_{H_2O} = nC_{p(H_2O(l))} \ln \frac{T_2}{T_1} + nC_{p(H_2O(g))} \ln \frac{T_2}{T_1} + n \frac{\Delta H}{T} \quad (13.E.18)$$

$$= (2 \times 75.4 \times \ln \frac{373}{298}) + (2 \times 36 \times \ln \frac{398}{373}) + (2 \times \frac{40680}{373}) = 256.6 \frac{\text{J}}{\text{K}} \quad (13.E.19)$$

$$\Delta S_{iron} = \frac{-94470 \text{ J}}{398 \text{ K}} = -237.4 \frac{\text{J}}{\text{K}} \quad (13.E.20)$$

$$\Delta S_{tot} = \Delta S_{H_2O} + \Delta S_{iron} = 19.2 \frac{\text{J}}{\text{K}} \quad (13.E.21)$$

Q19

A 181.49 g sample of lead at 97.0°C initially is added to a coffee cup calorimeter that contains 150.0 g water which is at 24.7°C. The equilibrium temperature is 29.4°C, assuming that there is no heat lost to the calorimeter or the environment. The molar heat capacity of lead ($C_p(\text{Pb})$) is $26.4 \text{ J K}^{-1} \text{ mol}^{-1}$ and that of water ($C_p(\text{H}_2\text{O})$) is $75.2 \text{ J K}^{-1} \text{ mol}^{-1}$. What is ΔS for the lead sample, ΔS for the water sample, and ΔS_{total} for this process?

Solution

Since this process is carried out at a constant pressure, and the temperature change for this process doesn't include a phase transition, the relationship between the ΔS and the ΔT of a system can be described as:

$$\Delta S = n c_p \ln \left(\frac{T_2}{T_1} \right) \quad (13.E.22)$$

Convert the temperatures to Kelvin:

$$T_{\text{equilibrium}} = (29.4 + 273.15) K = 302.55 K \quad (13.E.23)$$

$$T_{\text{initial, Pb}} = (97.0 + 273.15) K = 370.15 K \quad (13.E.24)$$

$$T_{\text{initial, H}_2\text{O}} = (24.7 + 273.15) K = 297.85 K \quad (13.E.25)$$

Calculate the amount of moles of the substance present:

$$n_{\text{Pb}} = 181.49 \text{ g Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} = 0.8759 \text{ mol Pb} \quad (13.E.26)$$

$$n_{\text{H}_2\text{O}} = 150.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 8.324 \text{ mol H}_2\text{O} \quad (13.E.27)$$

The given molar heat capacities:

$$C_{p, \text{Pb}} = 26.4 \frac{\text{J}}{\text{K} \cdot \text{mol}} \quad (13.E.28)$$

$$C_{p, \text{H}_2\text{O}} = 75.2 \frac{\text{J}}{\text{K} \cdot \text{mol}} \quad (13.E.29)$$

Substitute the known variables into the equation: $\Delta S = n c_p \ln \left(\frac{T_2}{T_1} \right)$

$$\Delta S_{\text{Pb}} = n c_{p, \text{Pb}} \ln \left(\frac{T_{\text{equilibrium}}}{T_{\text{initial, Pb}}} \right) \quad (13.E.30)$$

$$\Delta S_{\text{Pb}} = 0.8759 \text{ mol Pb} \times 26.4 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times \ln \left(\frac{302.55 \text{ K}}{370.15 \text{ K}} \right) = -4.66 \frac{\text{J}}{\text{K}} \quad (13.E.31)$$

$$\Delta S_{\text{H}_2\text{O}} = n c_{p, \text{H}_2\text{O}} \ln \left(\frac{T_{\text{equilibrium}}}{T_{\text{initial, H}_2\text{O}}} \right) \quad (13.E.32)$$

$$\Delta S_{\text{H}_2\text{O}} = 8.324 \text{ mol H}_2\text{O} \times 75.2 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times \ln \left(\frac{302.55 \text{ K}}{297.85 \text{ K}} \right) = 9.80 \frac{\text{J}}{\text{K}} \quad (13.E.33)$$

$$\Delta S_{\text{total}} = \Delta S_{\text{Pb}} + \Delta S_{\text{H}_2\text{O}} = (-4.66 + 9.80) \frac{\text{J}}{\text{K}} = 5.14 \frac{\text{J}}{\text{K}} \quad (13.E.34)$$

Q20

Copper has a heat capacity of $38.5 \text{ J K}^{-1} \text{ mol}^{-1}$, approximately independent of temperature between 0°C to 100°C . Calculate the enthalpy and entropy change of 5.00 moles of copper as it is cooled at atmospheric pressure from 100°C to 0°C .

Solution

$$\Delta H = q = n C_p \Delta T \quad (13.E.35)$$

$$= (5.00 \text{ mol}) (38.5 \frac{\text{J}}{\text{K} \cdot \text{mol}}) (273 \text{ K} - 373 \text{ K})$$

$$\Delta H = -19250 \text{ J}$$

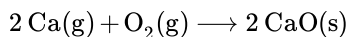
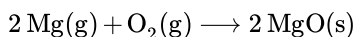
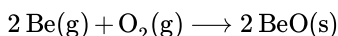
$$\Delta S = n C_p \ln \left(\frac{T_2}{T_1} \right) \quad (13.E.36)$$

$$= (38.5 \frac{\text{J}}{\text{K} \cdot \text{mol}}) \ln \left(\frac{273 \text{ K}}{373 \text{ K}} \right) (5.00 \text{ mol})$$

$$= -60.1 \frac{\text{J}}{\text{K}}$$

Q23

The **alkaline earth metals** react with oxygen to give the following compounds:

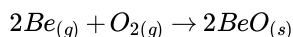


Compute ΔS for each reaction, and identify a periodic trend about the entropy.

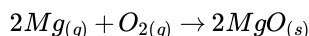
Solution

All the values you need to solve this problem are in the back of the Oxtoby textbook, so just find the numbers needed and use the formula:

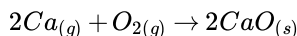
$$\sum S_{\text{products}}^{\circ} - \sum S_{\text{reactants}}^{\circ} = \Delta S_{\text{rxn}}^{\circ}$$



$$2(14.14) - (2(136.16) + 205.03) = -449.07 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$



$$2(26.92) - (2(148.54) + 205.03) = -448.27 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

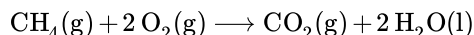


$$2(39.75) - (2(154.77) + 205.03) = -435.07 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

The entropy of the reaction decreases as you go up the periodic table.

Q27

Is the entropy change in the reaction positive, negative or zero and why?



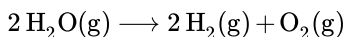
Hint: You don't need to actually calculate the change in entropy to determine whether the change in entropy is positive or negative. Think about it conceptually.

Solution

The answer is negative because the number of gas molecules decreases. Gas molecules have more entropy than liquid molecules since they have more energy in the form of degrees of freedom of motion (translational, rotational, and vibrational). Therefore, fewer gas molecules mean less entropy.

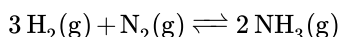
Q33

At 25.0 °C the reaction below is not spontaneous.



$$\text{with } \Delta G = +228.59 \frac{\text{kJ}}{\text{mol}}$$

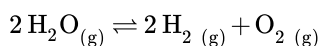
If the above reaction were coupled with the following nonspontaneous reaction, could it be made to proceed? Why or Why not?



$$\text{with } \Delta G = -16.48 \frac{\text{kJ}}{\text{mol}}$$

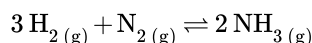
Solution

Coupling the nonspontaneous reaction



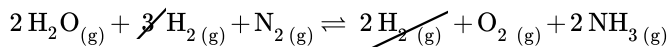
with $\Delta G = +228.59 \frac{\text{kJ}}{\text{mol}}$

for a spontaneous reaction (ΔG) is negative.



with $\Delta G = -16.48 \frac{\text{kJ}}{\text{mol}}$

yields



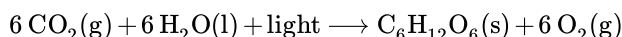
with $\Delta G = +212.11 \frac{\text{kJ}}{\text{mol}}$

Since ΔG is positive, we know the reaction is still not spontaneous after being coupled with a spontaneous reaction

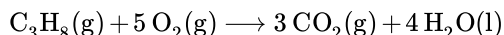
Q35A

A reaction at constant temperature and pressure is spontaneous if $\Delta G < 0$ and nonspontaneous if $\Delta G > 0$. Over what range of temperatures is each of the following processes spontaneous? Assume that all gases are at a pressure of 1 atm. (Hint: Use [Tables T1](#) to calculate ΔH and ΔS (assumed independent of temperature and equal to ΔH° and ΔS° , respectively, and then use the definition of ΔG).

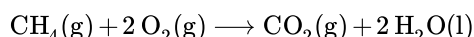
- a. Photosynthesis, a reaction of how plants produce food for themselves and animals, and convert carbon dioxide into water:



- b. The combustion reaction of propane, found in gas grills and some fireplaces:



- c. Methane burning in O_2 gas.



Solution

- a. First calculate ΔH° and ΔS° of the reaction $6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) + \text{light} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6 \text{O}_2(g)$ from the data in [Tables T1](#).

$$\Delta H^\circ = -1273.3 + (6 \times 0) - (6 \times -393.5) - (6 \times -285.8) = 2802.5 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S^\circ = 212.1 + (6 \times 205.2) - (6 \times 213.8) - (6 \times 70) = -259.5 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

Since the problem asks for the temperature range in which the reaction is spontaneous. The changeover from spontaneity to non-spontaneity occurs at $\Delta G^\circ = 0$. To find the temperature that makes $\Delta G^\circ = 0$, the relationship of $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ will be used. Remember to convert ΔS° to kJ mol^{-1} (or ΔH° to J mol^{-1}) so that the units cancel out properly.

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{2802.5 \frac{\text{kJ}}{\text{mol}}}{0.2595 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}} = 10799.6 \text{ K}$$

Because ΔH° and ΔS° are both positive, the reaction is spontaneous at temperatures above 10799.6 K.

Reviewer Note: The solution is incorrect here. Because $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$, the reaction is never spontaneous.

b. Perform similar calculations for the reaction $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \longrightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$

$$\Delta H^\circ = (3 \times -393.5) + (4 \times -285.83) + 103.8 - (5 \times 0) = -2220.02 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S^\circ = (3 \times 28) + (4 \times 70) - 270.3 - (5 \times 205.2) = -374.9 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{2220.02 \frac{\text{kJ}}{\text{mol}}}{0.3749 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}} = 5922 \text{ K}$$

Since ΔH° and ΔS° are both negative, the reaction is spontaneous below 5922 K.

c. The reaction $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$

$$\Delta H^\circ = (-393.5) + (2 \times -285.8) + 74.6 - (2 \times 0) = -890.5 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S^\circ = (28) + (2 \times 70) - 186.3 - (2 \times 205.2) = -242.9 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-890.5 \frac{\text{kJ}}{\text{mol}}}{-0.2429 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}} = 3666 \text{ K}$$

Since ΔH° and ΔS° are both negative, the reaction is spontaneous below 3666 K.

Q35B

Over what temperatures are these reactions spontaneous (under constant pressure and temperature)? You may need to use [Table 1](#).

- $\text{S}(\text{s, rhombic}) + \text{Zn}(\text{s}) \rightarrow \text{ZnS}(\text{s, sphalerite})$
- $2 \text{Cu}(\text{s}) + \text{Cl}_2 \rightarrow 2 \text{CuCl}(\text{s})$
- $4 \text{Al}(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{Al}_2\text{O}_3(\text{s})$

Answer

By calculating ΔH_{rxn} and ΔS_{rxn} under standard conditions and at 25°C , we can calculate the range of temperature in which ΔG is positive and therefore spontaneous. To calculate ΔH_{rxn} and ΔS_{rxn} , we use [Hess's Law](#), in which:

$$\Delta H_{\text{rxn}} = \sum nH_{\text{products}} - \sum nH_{\text{reactants}}$$

$$\Delta S_{\text{rxn}} = \sum nS_{\text{products}} - \sum nS_{\text{reactants}}$$

a)

$$\Delta H_{\text{rxn}} = -206.0 - (0 + 0) = -206.0 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S_{\text{rxn}} = 57.7 - (41.6 + 32.1) = -16 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

$$\Delta G_{\text{rxn}} = -206.0 - T(-0.016)$$

From here, we can set $T = 0$ because we know that ΔG must be < 0 to be a spontaneous reaction.

$$T < 12875 \text{ K}$$

b)

$$\Delta H_{\text{rxn}} = (2 \times -137.2) - (0 + 0) = -274.4 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S_{\text{rxn}} = (2 \times 86.2) - ((2 \times 33.2) + 223.1) = -117.1 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

$$\Delta G_{\text{rxn}} = -274.4 - T(-0.1171)$$

$$T < 2343.3\text{K}$$

c)

$$\Delta H_{\text{rxn}} = (2(-1675.7)) - (0 + 0) = -3351.4 \frac{\text{kJ}}{\text{mol}}$$

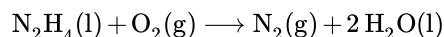
$$\Delta S_{\text{rxn}} = (2(50.92) - (4(28.3) + (3(205.2))) = -626.96 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

$$\Delta G_{\text{rxn}} = -3351.4 - T(-0.62696)$$

$$T < 5345.5\text{K}$$

Q37

Determine if the following reaction is spontaneous at 25°C by evaluating $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$ and $\Delta G^\circ_{\text{rxn}}$.



Solution

- $\Delta H^\circ_{\text{rxn}} = 0 + (2 \times -285.8) - 0 - 50.6 = 622.2 \frac{\text{kJ}}{\text{mol}}$
- $\Delta S^\circ_{\text{rxn}} = (2 \times 70.0) + 191.6 - 205.2 - 121.2 = 5.2 \frac{\text{J}}{\text{mol} \cdot \text{K}}$
- $\Delta G^\circ_{\text{rxn}} = -622.2 - (25 + 273.15)(0.0052) = -623.8 \frac{\text{kJ}}{\text{mol}}$

=> Spontaneous ($\Delta G^\circ_{\text{rxn}} < 0$)

Q39

A thermodynamic engine operates cyclically and reversibly between two temperatures reservoirs, absorbing heat from the high-temperature bath at 600 K and discarding heat to low-temperature bath at 300 K.

- What is the thermodynamic efficiency of the engine?
- How much heat is absorbed from the high-temperature bath if -1800 J of heat is discarded to the low-temperature bath during each cycle?
- How much work does the engine perform in one cycle of operation?

Solution

(a)

$$\text{Thermodynamic efficiency} = \frac{(T_1 - T_2)}{T_1}$$

$$\frac{(600 \text{ K} - 300 \text{ K})}{(600 \text{ K})} \times 100\% = 50\%$$

(b)

$$\frac{1800 \text{ J}}{50\%} = 3600 \text{ J}$$

(c)

$$-3600 \text{ J} \times 50\% = -1800 \text{ J}$$

Q41

Acetone ($\text{C}_3\text{H}_6\text{O}$) is a volatile liquid with a normal boiling point of 56°C and a molar enthalpy of vaporization of 29.1 kJ mol^{-1} . What is the molar entropy of vaporization of acetone under 1 atm of pressure?

Solution

First we need to write the equation relating entropy and enthalpy:

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

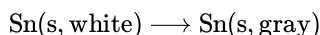
As a result of the process of normal boiling being at equilibrium $\Delta G = 0$ so all that needs to be done is T in Kelvin and ΔH_{vap} needs to be plugged in and then we solve for ΔS_{vap} :

$$0 = 29.1 \frac{\text{kJ}}{\text{mol}} - (329 \text{ K})(\Delta S_{\text{vap}})$$

$$\Delta S_{\text{vap}} = 88.45 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

Q53

Under standard conditions and 25°C , you have this reversible process



- Is the change in entropy (ΔS) for this reaction positive or negative? Calculate the change in entropy using Table T1.
- Calculate (ΔS) for the reaction if ΔH for this reaction is -2.1 kJ/mol .

Solution

For part a), we use the formula

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})$$

Plugging in the values from Table T1 gives us

$$\Delta S = 44.1 - 55.2 = -7.1 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

For part b), we use the formula for a reversible process

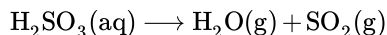
$$\Delta S = \frac{\Delta H}{T}$$

$$\Delta S = \frac{-2100 \text{ J/mol}}{298.15 \text{ K}}$$

$$\Delta S = -7.04 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

Q59

Compute the ΔG_f° for the following reaction the reaction. The ΔG_f° of $\text{H}_2\text{SO}_3(\text{aq})$ is $-537.81 \text{ kJ mol}^{-1}$, the ΔG_f° of $\text{SO}_2(\text{g})$ is $-300.19 \text{ kJ mol}^{-1}$, and the ΔG_f° of $\text{H}_2\text{O}(\text{g})$ is $-120.42 \text{ kJ mol}^{-1}$.



Solution

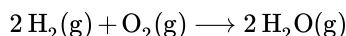
ΔG° for the reaction is equal to the sum of the G_f° for the products minus the sum of the G_f° for the reactants.

$$\Delta G^\circ = \left(-300.19 \frac{\text{kJ}}{\text{mol}} + -120.42 \frac{\text{kJ}}{\text{mol}} \right) - \left(-537.81 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta G^\circ = 117.2 \frac{\text{kJ}}{\text{mol}}$$

Q61

Professor Nesral wants to create some water through the combustion of hydrogen. This reaction is depicted as follows:



Is this reaction spontaneous? Prove it by calculating ΔG° at 298.15K. Suppose that Nesral asks his friend in El Azizia, Libya, where the temperature is around 57°C (330K), to perform the same reaction. Calculate the Gibbs energy for this value and compare it to ΔG° .

Relevant Information:

Entropy Values (S° ; $\frac{\text{J}}{\text{mol K}}$)

- Hydrogen: 130.6
- Water: 188.7
- Oxygen: 205.6

Enthalpy Values (H° ; $\frac{\text{kJ}}{\text{mol}}$)

- ΔH_f° Water: -241.826

Solution

From intuition, the equation shows that 3 moles of gas, 2 moles of H_2 and 1 mole of O_2 , are reacting to form 2 moles of H_2O gas. This is a decrease in entropy, which may hint at the reaction being non spontaneous. ΔG° should still be calculated to make sure.

The information provided is the entropic values of the product and reactants, and the enthalpy of water. If the ΔS° is calculated, then the ΔG° can also be found using the following equation:

$$\Delta G = \Delta H_{rxn}^\circ - T \Delta S_{rxn}^\circ.$$

Where ΔH_{rxn}° is the Heat and ΔS_{rxn}° is the entropy of the reaction under standard conditions (constant pressure), and T is temperature. Knowing that ΔS_{rxn}° is a state variable, it can be calculated as the difference between the sum of the entropy values of the products and reactants multiplied by their coefficients (This is known as Hess's Law). In other words,

$$\Delta S^\circ = \sum n_{products} \times S_{f,products}^\circ - \sum n_{reactants} \times S_{f,reactants}^\circ$$

From this, ΔS_{rxn}° can be calculated as such:

$$\begin{aligned} \Delta S^\circ &= \left(2 \times 188.7 \frac{\text{J}}{\text{mol K}} \right) - \left(\left[2 \times 130.6 \frac{\text{J}}{\text{mol K}} \right] + \left[205.6 \frac{\text{J}}{\text{mol K}} \right] \right) \\ &= -89.4 \frac{\text{J}}{\text{mol. K}} \end{aligned}$$

Since both H_2 and O_2 are in their natural states, the H_f° associated with them equals to zero. Since enthalpy (ΔH_{rxn}°) is also a state variable, it can be calculated with Hess's Law as well.

$$\begin{aligned} \Delta H^\circ &= \left(2 \times -241.826 \frac{\text{kJ}}{\text{mol}} \right) - \left(\left[0 \frac{\text{kJ}}{\text{mol}} \right] + \left[0 \frac{\text{kJ}}{\text{mol}} \right] \right) \\ \Delta H^\circ &= -483.652 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Plugging in these values, as well as the temperature, 298.15K will yield ΔG° .

$$\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T \Delta S_{rxn}^\circ.$$

$$\Delta G_{rxn}^\circ = -483.652 \frac{\text{kJ}}{\text{mol}} - 298.15 \text{K} \left(-0.0894 \frac{\text{kJ}}{\text{mol. K}} \right)$$

$$\Delta G_{rxn}^\circ = -456.99739 \frac{\text{kJ}}{\text{mol}}$$

The ΔG_{rxn} is therefore $-456.99739 \frac{kJ}{mol}$. This very negative value means that the reaction is DEFINITELY spontaneous. It also makes sense on a conceptual level because combustion reaction like these release a lot of heat, which means that the process is enthalpically driven! Calculating the ΔG_{rxn} at a different temperature, as mentioned in the problem, has the same method:

$$\Delta G_{rxn} = \Delta H_{rxn}^{\circ} - T \Delta S_{rxn}^{\circ}$$

$$\Delta G_{rxn} = -483.652 \frac{kJ}{mol} - 330 K \left(-0.0894 \frac{kJ}{mol \cdot K} \right)$$

$$\Delta G_{rxn} = -454.15 \frac{kJ}{mol}$$

In both situations the ΔG_{rxn} is very negative, but in the hotter climate it is slightly less so. What this shows is that, at a higher temperature the entropic factors contribute more to the Gibbs energy than at standard conditions. This showcases the temperature dependence of entropy. In another reaction that released less energy, this difference may have made the reaction non-spontaneous!

Abstract : Hess's Law to find ΔG_{rxn} .

Q63A

The concentration of sodium in the plasma is approximately 0.14 M. While in the fluid outside of the plasma, sodium concentration is about 0.5 M.

- In what direction will the sodium ions spontaneously move past the cell wall?
- The spontaneous process of movement in part a is called "passive transport". Movement in the opposite direction is called "active transport" and requires work to happen. Calculate the amount of free energy required to move 5 moles of Na^+ by active transport (non-spontaneous direction) at 273 K.

Solution

a) The Na^+ ions will spontaneously flow into the plasma because it flows from high to low concentration.

b) $\Delta G = nRT \ln \frac{c_2}{c_1}$ where c_2 is the destination of Na^+ after active transport occurs while c_1 is the original concentration of the Na^+ ions.

$$\Delta G = (5 \text{ mole}) \left(8.3145 \frac{J}{K \cdot mol} \right) (273 \text{ K}) \ln \frac{0.5}{0.14}$$

$$\Delta G = 14447.26 \text{ J}$$

Q63B

For a hypothetical nerve cell, the sodium ion concentration is 0.015 M outside the cell and 0.00045 M inside the cell. Active transport involves using proteins and chemical energy stored in ATP to move the ions in a thermodynamically unfavorable direction. Assuming that conditions in the cell allow the hydrolysis of a single ATP molecule to give 2.05×10^{-18} J of usable energy. How many molecules of ATP would be needed to move 0.005 moles of sodium ions using active transport at standard conditions? You can assume that the sodium ion concentrations remain constant.

Solution

To answer this question, the change of free energy is needed which means the following equation is needed

$$\Delta G = -RT \ln Q$$

$$R = 8.314 \frac{J}{mol \cdot K} \quad T = 298 K \quad Q = \frac{[Na^+]_{in}}{[Na^+]_{out}}$$

$$\Delta G = -8.314 \frac{J}{mol \cdot K} \times 298 K \times \ln \left(\frac{0.00045 M}{0.015 M} \right)$$

$$\Delta G = -2424 \frac{J}{mol} \times \ln(0.03) = 8688 \frac{J}{mol}$$

Now that we have the the free energy, we can determine the number of ATP molecules needed

$$8688 \frac{J}{mol} \times 0.005 \text{ mol} = 43.4 \text{ J}$$

$$\frac{43.4 \text{ J}}{2.05 \times 10^{-18} \text{ J molecule}^{-1}} = 2.119 \times 10^{19} \text{ ATP molecules}$$

Answer: 2.119×10^{19} ATP molecules

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