

1. Consider a system with energy levels that are equally spaced 5×10^{-18} J apart with the ground state at 0 J. If 10 particles are in the lowest level, 4 particles are in the first excited state, and 1 particle is in the second excited state, determine the internal energy, U , and the entropy, S , of the system. (Boltzmann's constant, $k = 1.381 \times 10^{-23}$ J/K) [2]
2. For a certain reaction to occur, a particle in a system has to have an energy of at least 3.0×10^{-20} J above the ground state. What fraction of the particles will have enough energy to react at 500 K? [1]
3. At what pressure will water boil at 298 K? The enthalpy of vaporization of water is 44.0 kJ mol^{-1} . $1 \text{ atm} = 1.01325 \text{ bar}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. [2]
4. One of the conditions of stable equilibrium is that $\frac{\partial^2 S}{\partial U^2} < 0$. Starting from $dS = \frac{dU}{T} + \frac{P}{T}dV$, prove that this implies $C_V > 0$. [2]
5. The composition of dry air is approximately 80% N_2 and 20% O_2 by volume. What is the molar entropy of mixing of air? Imagine that the two gases behave ideally and are at the same pressure initially. [1]
6. Given that at 298 K, the standard heats of formation (in kJ/mol) of CaCO_3 , CaO , and CO_2 are, respectively, -1207 , -635 , and -394 , while the entropies (in J/(mol K)) are, respectively, 89, 40, and 214. Is the decomposition of CaCO_3 to CaO and CO_2 thermodynamically spontaneous/unfeasible under standard conditions at 298 K? Justify. [1]
7. Would decreasing or increasing the temperature reverse the conclusion you arrived at in Q. 6? Justify with the help of a plot of the variation of the reaction Gibbs energy with temperature. [1]

1. Consider a system with energy levels that are equally spaced 5×10^{-18} J apart with the ground state at 0 J. If 10 particles are in the lowest level, 4 particles are in the first excited state, and 1 particle is in the second excited state, determine the internal energy, U , and the entropy, S , of the system. (Boltzmann's constant, $k = 1.381 \times 10^{-23}$ J/K) [2]

Answer:

$$U = \sum_i n_i \epsilon_i \quad \text{or} \quad \bar{U} = \sum_i p_i \epsilon_i \quad 0.5 \text{ mark}$$

$$U = (10 * 0 + 4 * 5 + 1 * 10) \times 10^{-18} \text{J} = 30 \times 10^{-18} \text{J} \quad 0.5 \text{ mark}$$

Alternatively, the average energy per molecule is also acceptable

$$\bar{U} = 2 \times 10^{-18} \text{J/molecule} \quad 0.5 \text{ mark}$$

$$W = \frac{15!}{10!4!1!} = 15015 \quad 0.5 \text{ mark}$$

$$S = k \ln W = 1.381 \times 10^{-23} \ln 15015 = 1.381 \times 10^{-23} \times 9.617 = 1.328 \times 10^{-22} \text{J K}^{-1} \quad 0.5 \text{ mark}$$

2. For a certain reaction to occur, a particle in a system has to have an energy of at least 3.0×10^{-20} J above the ground state. What fraction of the particles will have enough energy to react at 500 K? [1]

Answer:

$$f = e^{-\Delta E/kT} \quad 0.5 \text{ mark}$$

$$f = e^{-\frac{3.0 \times 10^{-20}}{1.381 \times 10^{-23} \times 500}} = 0.013 \quad 0.5 \text{ mark}$$

3. At what pressure will water boil at 298 K? The enthalpy of vaporization of water is 44.0 kJ mol^{-1} . 1 atm = 1.01325 bar, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. [2]

Answer:

$$\ln \frac{P_2}{P_1} = -\frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad 1 \text{ mark}$$

$$\ln \frac{P_2}{1.01325} = -\frac{44000 \text{ J/mol}}{8.314 \text{ J/(mol K)}} \left(\frac{1}{298 \text{ K}} - \frac{1}{373 \text{ K}} \right) \quad 0.5 \text{ mark}$$

$$\ln \frac{P_2}{1.01325} = -3.57 \implies P_2 = 28.5 \times 10^{-3} \text{ bar} = 0.0281 \text{ atm.} \quad 0.5 \text{ mark}$$

4. One of the conditions of stable equilibrium is that $\frac{\partial^2 S}{\partial U^2} < 0$. Starting from $dS = \frac{dU}{T} + \frac{P}{T}dV$, prove that this implies $C_V > 0$. [2]

Answer:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV = \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV$$

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T} \quad 0.5 \text{ mark}$$

Taking the differential of this equation

$$\frac{\partial^2 S}{\partial U^2} dU + \frac{\partial^2 S}{\partial V \partial U} dV = -\frac{dT}{T^2} \quad 0.5 \text{ mark}$$

$$\frac{\partial^2 S}{\partial U^2} = -\frac{1}{\left(\frac{\partial U}{\partial T} \right)_V T^2} = -\frac{1}{C_V T^2} \quad 1 \text{ mark}$$

5. The composition of dry air is approximately 80% N_2 and 20% O_2 by volume. What is the molar entropy of mixing of air? Imagine that the two gases behave ideally and are at the same pressure initially. [1]

Answer: Let the initial pressure of both the gases be P . The partial pressures of N_2 and O_2 after mixing are, respectively, $0.8P$ and $0.2P$, because the volume percentage is the same as mole percentage. If pressure changes from P_1 to P_2 the entropy change of an ideal gas is

$$\Delta S = -nR \ln \frac{P_2}{P_1} \quad 0.5 \text{ mark}$$

The entropy change of N_2 on going from P to $0.8P$ is $-0.8R \ln \frac{0.8P}{P}$ while that of O_2 on going from P to $0.2P$ is $-0.2R \ln \frac{0.2P}{P}$. Thus

$$\Delta S = -0.8R \ln 0.8 - 0.2R \ln 0.2 = 4.16 \text{ J K}^{-1} \quad 0.5 \text{ mark}$$

Alternative 1: The same argument may also be used with the volume. If the final volume is V , the initial volumes occupied by N_2 and O_2 are $0.8V$ and $0.2V$. The entropy change accompanying an isothermal expansion from V_1 to V_2 is

$$\Delta S = nR \ln \frac{V_2}{V_1} \quad 0.5 \text{ mark}$$

The rest of the argument is similar to that in the pressure case.

Alternative 2:

$$\Delta S = -R \sum_i n_i \ln x_i = -nR \sum_i x_i \ln x_i \quad 0.5 \text{ mark}$$

Hence,

$$\Delta S = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} (0.8 \ln 0.8 + 0.2 \ln 0.2)$$

$$\Delta S = -0.5 \times 8.314 \text{ J K}^{-1} = 4.16 \text{ J K}^{-1} \quad 0.5 \text{ mark}$$

6. Given that at 298 K, the standard heats of formation (in kJ/mol) of $CaCO_3$, CaO , and CO_2 are, respectively, -1207 , -635 , and -394 , while the entropies (in J/(mol K)) are, respectively, 89, 40, and 214. Is the decomposition of $CaCO_3$ to CaO and CO_2 thermodynamically spontaneous/unfeasible under standard conditions at 298 K? Justify. [1]

Answer:

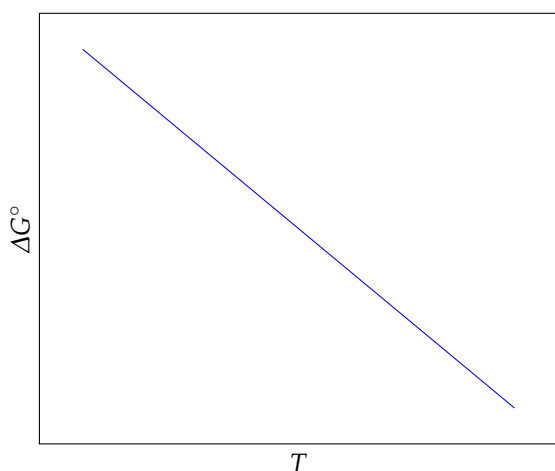
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -394000 - 635000 + 1207000 - 298 \times (40 + 214 - 89) = 128830 \text{ J/mol} \quad 0.5 \text{ mark}$$

Under conditions of constant T and P , the condition for thermodynamic spontaneity is $dG < 0$. Reaction is not spontaneous as ΔG° is positive. 0.5 mark.

7. Would decreasing or increasing the temperature reverse the conclusion you arrived at in Q. 6? Justify with the help of a plot of the variation of the reaction Gibbs energy with temperature. [1]

Answer: The reaction Gibbs energy is a decreasing function of temperature because $\left(\frac{\partial G}{\partial T}\right)_P = -\Delta S$ and ΔS is positive. [0.5 mark]



0.5 mark for graph

One would imagine that at higher temperature the reaction will become spontaneous.