

Chemistry 431
Problem Set 6
Fall 2023
Solutions

1. A Carnot engine operating between $T_l=0.^{\circ}\text{C}$ and T_h produces 1000. J of work on the surroundings per cycle. The entropy change during the high temperature, T_h , isothermal reversible expansion is 20.0 J K^{-1} . Calculate T_h , q_l and q_h for the cycle.

Answer:

$$w_{tot,surr} = q_l + q_h = 1000 \text{ J}$$

$$\frac{q_h}{T_h} = 20 \text{ J K}^{-1}$$

$$\frac{q_l}{T_l} + \frac{q_h}{T_h} = 0$$

$$\frac{q_l}{273 \text{ K}} = -\frac{q_h}{T_h}$$

$$q_l = -273 \text{ K} \frac{q_h}{T_h} = -273 \text{ K}(20 \text{ J K}^{-1}) = -5460 \text{ J}$$

$$q_h = 1000 \text{ J} - q_c = 6460 \text{ J}$$

$$T_h = -\frac{T_l}{q_l} q_h = 6460 \text{ J} \frac{\text{K}}{20 \text{ J}} = 323 \text{ K}$$

2. An ideal, reversible Carnot engine operates between a $50.^{\circ}\text{C}$ high temperature reservoir and a $10.^{\circ}\text{C}$ low temperature reservoir. If -200. Joules of work are done on the system in the high-temperature, reversible, isothermal expansion, calculate 1) the work done on the system for the low-temperature, reversible, isothermal compression and 2) the entropy changes for the system during the isothermal, reversible expansion and compression at $50.^{\circ}\text{C}$ and at $10.^{\circ}\text{C}$.

Answer:

$$\Delta U_1 = 0 \quad \text{so that} \quad q_h = -w_h = 200 \text{ J}$$

$$\Delta S_1 = \frac{q_h}{T_h} = \frac{200 \text{ J}}{323 \text{ K}} = 0.619 \text{ J K}^{-1}$$

$$\Delta S_2 = -\Delta S_1 = -0.619 \text{ J K}^{-1} = \frac{q_\ell}{T_\ell} = \frac{q_\ell}{283 \text{ K}} \quad q_\ell = -175. \text{ J}$$

$$w_\ell = -q_\ell = 175. \text{ J}$$

3. Three moles of an ideal monatomic gas occupy a 5.0 liter cylinder fitted with a piston at 20.0°C. Calculate ΔS for the system, surroundings and universe if the gas is compressed reversibly and isothermally to a final volume of 1.0 liters.

Answer:

$$\Delta S_{sys} = nR \ln \frac{V_2}{V_1} = (3 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{1}{5} = -40.14 \text{ J K}^{-1}$$

$$\Delta S_{univ} = 0$$

$$\Delta S_{surr} = 40.14 \text{ J K}^{-1}$$

4. Three moles of an ideal monatomic gas occupy a 5.0 liter cylinder with the same initial conditions as problem 3. Calculate ΔS for the system, surroundings and universe if the gas is compressed isothermally against a constant external pressure of 100. bar to a final volume of 1.0 liters.

Answer:

$$\Delta S_{sys} = -40.14 \text{ J mol}^{-1}\text{K}^{-1}$$

because the initial and final states are the same as in the previous problem.

$$\Delta U_{sys} = q_{sys} + w_{sys} = 0$$

$$q_{sys} = -w_{sys} = P_{ext}\Delta V$$

$$= (100 \text{ bar})(1 \text{ L} - 5 \text{ L}) \left(\frac{8.3144 \text{ J}}{0.08314 \text{ L bar}} \right) = -40001 \text{ J}$$

$$q_{surr} = 40001 \text{ J}$$

$$\Delta S_{surr} = \frac{40001 \text{ J}}{293 \text{ K}} = 136.5 \text{ J K}^{-1}$$

$$\Delta S_{univ} = 136.5 \text{ J K}^{-1} - 40.14 \text{ J K}^{-1} = 96.36 \text{ J K}^{-1}$$

5. Three moles of an ideal monatomic gas occupy a 5.0 liter cylinder with the same initial conditions as problem 3. Calculate ΔS for the system, surroundings and universe if the gas is compressed reversibly and adiabatically to a final volume of 1.0 liters.

Answer:

$$q_{sys} = q_{rev} = 0$$

Then

$$\Delta S_{sys} = \Delta S_{surr} = \Delta S_{univ} = 0$$

6. Three moles of an ideal monatomic gas occupy a 5.0 liter cylinder with the same initial conditions as problem 3. Calculate ΔS for the system, surroundings and universe if the gas is compressed adiabatically against a constant external pressure of 100. bar to a final volume of 1.0 liters.

Answer:

$$\Delta U = w = -P_{ext}\Delta V = -100 \text{ bar}(1 \text{ L} - 5 \text{ L}) = 400 \text{ L bar}$$

$$\begin{aligned}
C_V \Delta T &= \Delta U \\
\frac{3}{2}(3 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(T_f - 293 \text{ K}) &= 400 \text{ L bar} \\
T_f &= 1362 \text{ K} \\
\Delta S_{sys} &= nR \ln \frac{V_f}{V_i} + C_V \ln \frac{T_f}{T_i} \\
&= (3 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \left[\ln \frac{1}{5} + \frac{3}{2} \ln \frac{1362}{293} \right] = 17.34 \text{ J K}^{-1} \\
\Delta S_{surr} &= 0 \\
\Delta S_{univ} &= 17.34 \text{ J K}^{-1}
\end{aligned}$$

7. Calculate ΔS for the system, surroundings and universe when 2.0 moles of an ideal diatomic gas at 25.0°C and a pressure of 10.0 bar are expanded adiabatically against a constant external pressure of 1.0 bar until equilibrium is reached.

Answer:

$$\begin{aligned}
\Delta U &= w = C_V \Delta T \\
-(1 \text{ bar}) \left(\frac{nRT_f}{1 \text{ bar}} - \frac{nR(298 \text{ K})}{10 \text{ bar}} \right) &= \frac{5}{2}nR(T_f - 298 \text{ K}) \\
-(T_f - 298 \text{ K}) &= \frac{5}{2}T_f - 745 \text{ K} \\
T_f &= 221 \text{ K} \\
\Delta S_{sys} &= C_P \ln \frac{T_f}{T_i} + nR \ln \frac{P_i}{P_f} \\
&= nR \left(\frac{7}{2} \ln \frac{T_f}{T_i} + \ln \frac{P_i}{P_f} \right) \\
&= (2 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \left(\frac{7}{2} \ln \frac{221}{298} + \ln \frac{10}{1} \right) = 20.9 \text{ JK}^{-1} \\
\Delta S_{surr} &= 0 \\
\Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} = 20.9 \text{ JK}^{-1}
\end{aligned}$$

8. Calculate ΔS for the system, surroundings and universe when 5.0 grams of H₂ gas are:

- (a) cooled reversibly at constant pressure from 100.°C to 0.°C.

Answer:

$$\begin{aligned}
\Delta S_{sys} &= \int \frac{dq_{rev}}{T} = \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \ln \frac{T_f}{T_i} \\
&= \frac{7}{2} \left(\frac{5.0 \text{ g}}{2.016 \text{ g mol}^{-1}} \right) (8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{273}{373} = -22.52 \text{ J K}^{-1} \\
\Delta S_{univ} &= 0 \quad \Delta S_{surr} = 22.52 \text{ J K}^{-1}
\end{aligned}$$

- (b) cooled irreversibly at constant pressure in a refrigerator thermostated to 0.°C from 100.°C.

Answer:

$$\Delta S_{sys} = -22.52 \text{ J K}^{-1}$$

$$q_{sys} = C_p \Delta T = \frac{7}{2} \left(\frac{5.0 \text{ g}}{2.016 \text{ g mol}^{-1}} \right) (8.3144 \text{ J mol}^{-1} \text{K}^{-1})(-100 \text{ K}) = -7217 \text{ J}$$

$$\Delta S_{surr} = \frac{7217 \text{ J}}{273 \text{ K}} = 26.44 \text{ J K}^{-1}$$

$$\Delta S_{univ} = 26.44 \text{ J K}^{-1} - 22.52 \text{ J K}^{-1} = 3.92 \text{ J K}^{-1}$$

9. When 3.0 moles of an ideal monatomic gas are placed in a constant volume 10.0 L container, the initial temperature is found to be 50.0°C. The gas is then placed in a refrigerator with the thermostat set to -25.0°C, and the system is allowed to come to thermal equilibrium. Calculate ΔS for the system, surroundings and universe.

Answer:

$$\Delta S_{sys} = C_V \ln \frac{T_f}{T_i} = \frac{3}{2} n R \ln \frac{T_f}{T_i}$$

$$= \frac{3}{2} (3.0 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1}) \ln \frac{248}{323} = -9.88 \text{ J K}^{-1}$$

$$q_{sys} = C_V \Delta T = \frac{3}{2} n R \Delta T$$

$$= \frac{3}{2} (3.0 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(-75.0 \text{ K}) = -2806 \text{ J}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}} = \frac{2806 \text{ J}}{248 \text{ K}} = 11.31 \text{ J K}^{-1}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} = 1.43 \text{ J K}^{-1}$$

10. When a bulb of constant volume containing 10.0 grams of O₂ gas at 298K is placed in an oven with an unknown but fixed temperature, the entropy change for the oxygen gas after thermal equilibrium is reached is found to be 2.00 J K⁻¹. Calculate the entropy change for the surroundings.

Answer

$$\Delta S_{sys} = C_V \ln \frac{T_f}{T_i}$$

$$2.00 \text{ J K}^{-1} = \frac{5}{2} \left(\frac{10.0 \text{ g}}{32.0 \text{ g mol}^{-1}} \right) (8.3144 \text{ J mol}^{-1} \text{K}^{-1}) \ln \frac{T_f}{298 \text{ K}}$$

$$T_f = 405. \text{ K}$$

$$q_{sys} = C_V \Delta T = \frac{5}{2} \left(\frac{10.0 \text{ g}}{32.0 \text{ g mol}^{-1}} \right) (8.3144 \text{ J mol}^{-1} \text{K}^{-1})(405. \text{ K} - 298. \text{ K}) = 695. \text{ J}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}} = \frac{-695. \text{ J}}{405. \text{ K}} = -1.72 \text{ J K}^{-1}$$

11. At an initial temperature of $T = 350\text{K}$ and at a pressure of 3.00 bar, 2.00 moles of an ideal monatomic gas are first placed in a refrigerator with the thermostat set to $T = 273\text{K}$ and allowed to come to equilibrium at constant pressure. The gas is then moved to a constant temperature bath with the thermostat set to 298 K again at a pressure of 3.00 bar and is allowed to come to equilibrium at constant pressure. Calculate ΔS for the system, surroundings and universe for the overall two-step process.

Answer:

$$\begin{aligned}\Delta S_{\text{system}} &= nR \ln \frac{P_i}{P_f} + C_P \ln \frac{T_f}{T_i} = C_P \ln \frac{T_f}{T_i} \\ &= \frac{5}{2} nR \ln \frac{T_f}{T_i} = \frac{5}{2} (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{298}{350} = -6.69 \text{ J K}^{-1}\end{aligned}$$

$$q_{\text{system},1} = C_P \Delta T$$

$$= \frac{5}{2} (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(273 \text{ K} - 350 \text{ K}) = -3200 \text{ J}$$

$$\Delta S_{\text{surroundings},1} = \frac{-q_{\text{system},1}}{T_{\text{surroundings}}} = \frac{3200 \text{ J}}{273 \text{ K}} = 11.71 \text{ J K}^{-1}$$

$$q_{\text{system},2} = C_P \Delta T$$

$$= \frac{5}{2} (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K} - 273 \text{ K}) = 1040 \text{ J}$$

$$\Delta S_{\text{surroundings},2} = \frac{-q_{\text{system},2}}{T_{\text{surroundings}}} = \frac{-1040 \text{ J}}{298 \text{ K}} = -3.49 \text{ J K}^{-1}$$

$$\Delta S_{\text{surroundings}} = \Delta S_{\text{surroundings},1} + \Delta S_{\text{surroundings},2} = 8.22 \text{ J K}^{-1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 1.53 \text{ J K}^{-1} > 0$$

as it must be.

12. A brick of heat capacity C_1 at temperature T_1 is placed on a brick of heat capacity C_2 at temperature T_2 . The bricks are placed in contact adiabatically, and heat flows until equilibrium is reached.

- (a) Find an expression for ΔS for the process.

Answer:

$$q = C_1(T_f - T_1) + C_2(T_f - T_2) = 0$$

$$T_f = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2}$$

$$\Delta S = C_1 \ln \frac{T_f}{T_1} + C_2 \ln \frac{T_f}{T_2}$$

(b) If $C_1=3000. \text{ J K}^{-1}$, $C_2=5000. \text{ J K}^{-1}$, $T_1=0.^{\circ}\text{C}$ and $T_2=100.^{\circ}\text{C}$, find ΔS .

Answer:

$$T_f = \frac{(3000 \text{ J K}^{-1})(273 \text{ K}) + (5000 \text{ J K}^{-1})(373 \text{ K})}{8000 \text{ J K}^{-1}} = 335.5 \text{ K}$$

$$\Delta S = 3000 \text{ J K}^{-1} \ln \frac{335.5}{273} + 5000 \text{ J K}^{-1} \ln \frac{335.5}{373} = 88.67 \text{ J K}^{-1}$$

13. A conducting container of fixed volume contains 2.00 moles of an ideal monatomic gas at a pressure of $P = 2.50 \text{ bar}$ and an initial temperature of 275. K. The container with the gas is placed in an oven with the thermostat set to 373. K, and the system is allowed to come to equilibrium. The container is then placed in a refrigerator with the thermostat set to the initial temperature of 275. K and allowed to come to equilibrium. Calculate ΔS for the system, surroundings and universe for the overall process.

Answer:

$$\Delta S_{sys} = C_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i} = 0, \quad \text{because } T_i = T_f \quad \text{and} \quad V_i = V_f$$

$$q_{sys,1} = C_V(T_f - T_i) = \frac{3}{2}nR(T_f - T_i)$$

$$= \frac{3}{2}(2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(373. \text{ K} - 275. \text{ K}) = 2444. \text{ J}$$

$$\Delta S_{surr,1} = \frac{-q_{sys,1}}{T_{surr}} = -\frac{2444. \text{ J}}{373. \text{ K}} = -6.55 \text{ J K}^{-1}$$

$$q_{sys,2} = -q_{sys,1} = -2444. \text{ J}$$

$$\Delta S_{surr,2} = \frac{-q_{sys,2}}{T_{surr}} = \frac{2444. \text{ J}}{275. \text{ K}} = 8.89 \text{ J K}^{-1}$$

$$\Delta S_{surr} = \Delta S_{surr,1} + \Delta S_{surr,2} = 2.34 \text{ J K}^{-1} = \Delta S_{universe} > 0$$

14. The molar, constant-pressure heat capacity of liquid water is $75.24 \text{ J mol}^{-1}\text{K}^{-1}$ and can be assumed to be temperature independent. Calculate ΔS for the system, surroundings and universe when 20.0 g of liquid water at 25.0°C are placed in a refrigerator with the thermostat set to 10.0°C at fixed pressure.

Answer:

$$n = \frac{20.0 \text{ g}}{18.0 \text{ g mol}^{-1}} = 1.11 \text{ mol}$$

$$\Delta S_{system} = \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = \int_{T_i}^{T_f} \frac{C_P dT}{T} = C_P \ln \frac{T_f}{T_i} = (1.11 \text{ mol})(75.24 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{283}{298} = -4.31 \text{ J K}^{-1}$$

$$q_{system} = C_P \Delta T = (1.11 \text{ mol})(75.24 \text{ J mol}^{-1}\text{K}^{-1})(-15. \text{ K}) = -1253 \text{ J}$$

$$\Delta S_{surroundings} = \frac{-q_{system}}{T_{surroundings}} = \frac{1253 \text{ J}}{283 \text{ K}} = 4.43 \text{ J K}^{-1}$$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0.117 \text{ J K}^{-1}$$

15. The molar heat capacity of liquid water is $75.24 \text{ J mol}^{-1}\text{K}^{-1}$ and can be assumed to be temperature independent. Calculate ΔS and $\int \dot{d}q/T$ for the system when 10.0 grams of liquid water at 10.0°C and 30.0 grams of liquid water at 50.0°C are mixed in an isolated tank. Verify that the Clausius inequality is satisfied.

Answer:

$$n_1 = \frac{10.0 \text{ g}}{18.0 \text{ g mol}^{-1}} = 0.556 \text{ mol} \quad n_2 = 3n_1 = 1.67 \text{ mol}$$

$$(75.24 \text{ J mol}^{-1}\text{K}^{-1})[(0.556 \text{ mol})(T_f - 283 \text{ K}) + (1.67 \text{ mol})(T_f - 323 \text{ K})] = 0$$

$$T_f = 313 \text{ K}$$

$$\Delta S = (75.24 \text{ J mol}^{-1}\text{K}^{-1}) \left[(0.556 \text{ mol}) \ln \left(\frac{313}{283} \right) + (1.67 \text{ mol}) \left(\frac{313}{323} \right) \right] = 0.263 \text{ J K}^{-1}$$

Adiabatic so

$$\int \frac{\dot{d}q}{T} = 0$$

and

$$\Delta S \geq \int \frac{\dot{d}q}{T}$$

as required.

16. The constant pressure and volume heat capacities of liquid mercury are essentially identical and equal to $28.0 \text{ J mol}^{-1}\text{K}^{-1}$. Calculate ΔS for the system when 20.0 g of Hg at 15.0°C are mixed with 50.0 g of Hg at 40.0°C in an isolated tank. You can assume the heat capacity is temperature independent.

Answer:

$$q = 0 \quad \text{let } c = \text{the heat capacity per gram of Hg.}$$

Then

$$c[20.0 \text{ g}(T_f - 288. \text{ K}) + 50.0 \text{ g}(T_f - 313. \text{ K})] = 0 \quad T_f = 306. \text{ K}$$

$$n_1 = \frac{20.0 \text{ g}}{200.6 \text{ g mol}^{-1}} = 9.97 \times 10^{-2} \text{ mol}$$

$$n_2 = \frac{50.0 \text{ g}}{200.6 \text{ g mol}^{-1}} = 0.249 \text{ mol}$$

$$\Delta S = C_1 \ln \frac{T_f}{T_1} + C_2 \ln \frac{T_f}{T_2}$$

$$= 28.0 \text{ J mol}^{-1}\text{K}^{-1} \left[(9.97 \times 10^{-2} \text{ mol}) \left(\ln \frac{306}{288} \right) + (0.249 \text{ mol}) \left(\ln \frac{306}{313} \right) \right] = 1.15 \times 10^{-2} \text{ J K}^{-1}$$

17. The heat capacity of ice is $2.06 \text{ J g}^{-1}\text{K}^{-1}$ and can be assumed to be independent of temperature. 10.0 g of ice at -5.0°C and 20.0 g of ice at -30.0°C are put in thermal contact in an isolated tank and allowed to reach thermal equilibrium. Calculate the entropy change for the process.

Answer: Let C be the heat capacity of ice in $\text{J g}^{-1}\text{K}^{-1}$. The final temperature is found using

$$10C(T_f - 268 \text{ K}) + 20C(T_f - 243 \text{ K}) = 0$$

or

$$T_f = 251.3 \text{ K}$$

Then

$$\Delta S = (2.06 \text{ J g}^{-1}\text{K}^{-1}) \left((10 \text{ g}) \ln \frac{251.3}{268} + (20 \text{ g}) \ln \frac{251.3}{243} \right) = 0.058 \text{ JK}^{-1}$$