Chemistry 431 Problem Set 6 Fall 2023

- 1. A Carnot engine operating between T_l =0.°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.
- 2. An ideal, reversible Carnot engine operates between a 50.°C high temperature reservoir and a 10.°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.°C and at 10.°C.
- 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.
- 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.
- 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.
- 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.
- 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.
- 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.

- (b) cooled irreversibly at constant pressure in a refrigerator thermostated to 0.°C from 100.°C.
- 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.
- 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.
- 11. At an initial temperature of $T=350 \mathrm{K}$ 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 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.
- 12. A brick of heat capacity C_1 at temperature T_1 is paced 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.
 - (b) If C_1 =3000. J K⁻¹, C_2 =5000. J K⁻¹, T_1 =0.°C and T_2 =100.°C, find ΔS .
- 13. A conducting container of fixed volume contains 2.00 moles of an ideal monatomic gas at a pressure of P=2.50 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.
- 14. The molar, constant-pressure heat capacity of liquid water is 75.24 J mol $^{-1}$ 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.
- 15. The molar heat capacity of liquid water is 75.24 J mol⁻¹K⁻¹ and can be assumed to be temperature independent. Calculate ΔS and $\int dq/T$ 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.

- 16. The constant pressure and volume heat capacities of liquid mercury are essentially identical and equal to 28.0 J mol⁻¹K⁻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.
- 17. The heat capacity of ice is $2.06~\rm J~g^{-1}K^{-1}$ 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.