## Chemistry 431 <br> Problem Set 6 <br> Fall 2023

1. A Carnot engine operating between $T_{l}=0 .{ }^{\circ} \mathrm{C}$ 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 $20.0 \mathrm{~J} \mathrm{~K}^{-1}$. Calculate $T_{h}, q_{l}$ and $q_{h}$ for the cycle.
2. An ideal, reversible Carnot engine operates between a $50 .{ }^{\circ} \mathrm{C}$ high temperature reservoir and a $10 .{ }^{\circ} \mathrm{C}$ 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 $50 .{ }^{\circ} \mathrm{C}$ and at $10 .{ }^{\circ} \mathrm{C}$.
3. Three moles of an ideal monatomic gas occupy a 5.0 liter cylinder fitted with a piston at $20.0^{\circ} \mathrm{C}$. Calculate $\Delta S$ 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 $\Delta S$ 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 $\Delta S$ 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 $\Delta S$ 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 $\Delta S$ for the system, surroundings and universe when 2.0 moles of an ideal diatomic gas at $25.0^{\circ} \mathrm{C}$ 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 $\Delta S$ for the system, surroundings and universe when 5.0 grams of $\mathrm{H}_{2}$ gas are:
(a) cooled reversibly at constant pressure from $100 .{ }^{\circ} \mathrm{C}$ to $0 .{ }^{\circ} \mathrm{C}$.
(b) cooled irreversibly at constant pressure in a refrigerator thermostated to $0 .{ }^{\circ} \mathrm{C}$ from $100 .{ }^{\circ} \mathrm{C}$.
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 $50.0^{\circ} \mathrm{C}$. The gas is then placed in a refrigerator with the thermostat set to $-25.0^{\circ} \mathrm{C}$, and the system is allowed to come to thermal equilibrium. Calculate $\Delta S$ for the system, surroundings and universe.
10. When a bulb of constant volume containing 10.0 grams of $\mathrm{O}_{2}$ gas at 298 K 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 $2.00 \mathrm{~J} \mathrm{~K}^{-1}$. Calculate the entropy change for the surroundings.
11. At an initial temperature of $T=350 \mathrm{~K}$ and at a pressure of $3.00 \mathrm{bar}, 2.00$ 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 $\Delta S$ 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 $\Delta S$ for the process.
(b) If $C_{1}=3000 . \mathrm{J} \mathrm{K}^{-1}, C_{2}=5000 . \mathrm{J} \mathrm{K}^{-1}, T_{1}=0 .{ }^{\circ} \mathrm{C}$ and $T_{2}=100 .{ }^{\circ} \mathrm{C}$, find $\Delta S$.
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 $373 . \mathrm{K}$, 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 $\Delta S$ for the system, surroundings and universe for the overall process.
14. The molar, constant-pressure heat capacity of liquid water is $75.24 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ and can be assumed to be temperature independent. Calculate $\Delta S$ for the system, surroundings and universe when 20.0 g of liquid water at $25.0^{\circ} \mathrm{C}$ are placed in a refrigerator with the thermostat set to $10.0^{\circ} \mathrm{C}$ at fixed pressure.
15. The molar heat capacity of liquid water is $75.24 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ and can be assumed to be temperature independent. Calculate $\Delta S$ and $\int \not \partial q / T$ for the system when 10.0 grams of liquid water at $10.0^{\circ} \mathrm{C}$ and 30.0 grams of liquid water at $50.0^{\circ} \mathrm{C}$ 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 $28.0 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$. Calculate $\Delta S$ for the system when 20.0 g of Hg at $15.0^{\circ} \mathrm{C}$ are mixed with 50.0 g of Hg at $40.0^{\circ} \mathrm{C}$ in an isolated tank. You can assume the heat capacity is temperature independent.
17. The heat capacity of ice is $2.06 \mathrm{~J} \mathrm{~g}^{-1} \mathrm{~K}^{-1}$ and can be assumed to be independent of temperature. 10.0 g of ice at $-5.0^{\circ} \mathrm{C}$ and 20.0 g of ice at $-30.0^{\circ} \mathrm{C}$ are put in thermal contact in an isolated tank and allowed to reach thermal equilibrium. Calculate the entropy change for the process.
