Chemistry 2290, Winter 2012, G. Schreckenbach
Practice problems –4–

Second Law: Calculation of Entropy Changes

Practice problems from Laidler/ Meiser
(Problems adapted from Laidler, Meiser, Sanctuary, Physical Chemistry, 4th ed., Houghton Mifflin)

LM18. Calculate the entropies of vaporization (in units of J K^{-1} mol^{-1}) of the following substances from the following data:

	Boling Point (K)	$\Delta_{vap}H$ (kJ mol^{-1})
C_6H_6	353	30.8
$CHCl_3$	334	29.4
H_2O	373	40.6
C_2H_5OH	351	38.5

In terms of the structure of the liquids, suggest reasons for the higher values observed for the last two compounds in the table.

LM19. One mole (1.00 mol) of a monoatmic ideal gas ($C_{V,m}$ = 3/2R) is heated (a) at constant pressure, and (b) at constant volume from 298K to 353K. Calculate ΔS for the system in each case.

LM20. One mole each of N_2 and O_2 and 1/2 mol of H_2, at 25.0ºC and 1.00 atm pressure, are mixed isothermally; the final total pressure is 1.00 atm. Calculate ΔS, on the assumption of ideal behavior.

LM21. Initially 1 mol of oxygen gas is contained in a 1-Liter vessel, and 5 mol of nitrogen gas are in a 2-Liter vessel; the two vessels are connected by a tube with a stopcock. If the stopcock is opened and the gases mix, what is the entropy change?

LM22. Calculate the entropy of mixing per mole of air, taking the composition by volume to be 79% N_2, 20% O_2, and 1% Ar.

LM23. (a) One mole of a monoatomic ideal gas ($C_{V,m}$ = 3/2R) at 25ºC is allowed to expand reversibly and isothermally from 1 dm^3 to 10 dm^3. What is ΔS for the gas, and what is ΔS for the surroundings?
(b) The same gas is expanded adiabatically and irreversibly from 1 dm^3 to 10 dm^3 with no work done. What is the final temperature of the gas? What is ΔS for the gas, and what is ΔS for the surroundings? What is the net ΔS?

LM24. One mole of liquid water at 0.00ºC and 1.00 atm pressure is turned into steam at 100.0 ºC and 1.00 atm pressure by the following two paths:

(a) Heated at constant pressure to 100.0 ºC and allowed to boil into steam ($\Delta_{vap}H^o$ = 40.67 kJ mol^{-1} at this temperature.)

(b) Pressure lowered to 0.00602 atm so that water evaporates to steam at 0.00ºC ($\Delta_{vap}H^o$ = 44.92 kJ mol^{-1} at this temperature), heated at the constant pressure of 0.00602 atm to 100.0 ºC and compressed at 100.0 ºC to 1 atm pressure.

Calculate the entropy along each path and verify that they are the same, thus verifying that ΔS^o is a state function. Use $C_{p,m}$ = 75.48 J K^{-1} mol^{-1} for liquid water, and $C_{p,m}$ = 30.54 J K^{-1} mol^{-1} for steam (assumed constant – this is a simplification).

LM25. Initially 5.0 mol of an ideal gas with $C_{V,m}$ = 12.5 J K^{-1} mol^{-1} are at a volume of 5.00 dm^3 and a temperature of 300K. If the gas is heated to 373K and the volume changed to 10.0 dm^3, what is the entropy change?

LM26. One mole of water (1.00 mol) is placed in surroundings at –3.0 ºC, but at first it does not freeze (it remains as supercooled water). Suddenly it freezes. Calculate the entropy change in the system during freezing, making use of the following data: $C_{p,m}$ (water) = 75.3 J K^{-1} mol^{-1}, $C_{p,m}$ (ice) = 37.7 J K^{-1} mol^{-1}, $\Delta_f H$ (ice → water) = 6.02 kJ mol^{-1} at 0ºC. The two heat capacities can be taken as independent of temperature. Also, calculate the entropy change in the surroundings and the net entropy change in the system and surroundings.

LM27. One mole of liquid water at 0.0ºC is placed is placed in a freezer having a temperature of –12.0 ºC. The water freezes and the ice cools to –12.0 ºC. Making use of the data in Problem LM26, calculate the entropy change in the system, the surroundings (the freezer), and the net entropy change.

LM28. Two moles (2.00 mol) of water at 60 ºC are added to 4.00 mol at 20 ºC. Calculate the entropy change, assuming that there is no loss of heat to the surroundings. Use the value for the heat capacity of water from Problem LM26.