Problem set 12

Due June 4, 2025

1. Consider the reaction of 1 mole of gaseous fluorine-19 ($^{19}F_2$) with 1 mole of gaseous chlorine-35 ($^{35}Cl_2$) to give 2 moles of gaseous chlorine fluorine ($^{35}Cl^{19}F$).

$$^{19}F_2 +^{35} Cl_2 \rightleftharpoons 2^{35}Cl^{19}F$$

   (a) Derive the formula for the energy of this reaction. The dissociation energies of the molecules involved with zero-point oscillation energies subtracted ($D_\circ$) and their characteristic oscillation temperatures (Θ_ν) are listed in the table below.

Molecule	$D_\circ$ [kcal/mol]	Θ_ν [K]
$^{19}F_2$	37.0	1284
$^{35}Cl_2$	57.3	808
$^{35}Cl^{19}F$	59.5	1115

   (b) Make a plot of the energy of this reaction as a function of temperature from $T = 300$ K to $T = 2000$ K.

2. Consider the isotope-exchange reaction between $^{14}N_2$ and $^{15}N_2$.

$$^{14}N_2 +^{15} N_2 \rightleftharpoons 2^{14}N^{15}N$$

   (a) Based on the formula for the equilibrium constant for the isotopic-exchange reaction between hydrogen and deuterium to form hydrogen-deuterium, derive the formula for the gas-phase equilibrium constant of this reaction. The characteristic vibrational temperature of the $^{14}N_2$ molecule is $\Theta_\nu = 3374$ K.

   (b) Make the Arrhenius plot $\log K = f(1/T)$.

   (c) The data of the time course of the $^{14}N_2$ – $^{15}N_2$ isotope-exchange reaction catalyzed by iron and methylamine (Joris & Taylor, *J. Chem. Phys.*, 7, 893, 1939) at two temperatures are in the table below. Check if these data approach those corresponding to the calculated equilibrium constant at long times. Comment on the results.

T [°C]	time [h]	quantity/1000 units of $^{14}N_2$	
		$^{14}N^{15}N$	$^{15}N_2$
465	2	100.5	51.50
	17	125.8	39.00
	37	163.0	22.60
	60	194.0	14.00
500	2	108.0	48.00
	8	142.0	38.00
	21	184.0	20.00
	26	197.5	17.40
	35	202.0	13.40
	46	207.0	13.25

Hint: You can compute the apparent "equilibrium constant" at each time and compare the consecutive values with those calculated from the first principles at each of the two temperatures.