Problem set 11

Due May 26, 2026

1. Consider the reaction of 1 mole of gaseous fluorine-19 ($^{19}F_2$) with 1 mole of gaseous xenon (^{132}Xe) to give 1 mole of gaseous xenon difluoride ($^{132}Xe^{19}F_2$) (a symmetric linear molecule).

$$^{132}\mathrm{Xe} +^{19} \mathrm{F}_2 \rightleftharpoons^{132} \mathrm{Xe}^{19}\mathrm{F}_2$$

   (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 vibrational wave numbers ($\overline{\nu}$), along with the degeneracies of the respective vibrational modes, are listed in the table below.

Molecule	$D_\circ$ [kJ/mol]	$\overline{\nu}$ [cm^{-1}]
$^{19}F_2$	154.8	894
$^{132}Xe^{19}F_2$	267.8	214 (2), 515 (1), 555 (1)

   (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 $^{15}N_2$.

$$^{14}\mathrm{N}_2 +^{15} \mathrm{N}_2 \rightleftharpoons 2^{14}\mathrm{N}^{15}\mathrm{N}$$

   (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 $\log K = f(1/T)$.

3. 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.

   (a) Calculate the fractions of all three dinitrogen species at each point.

(b) Insert the calculated fractions into the expression for the isotope-exchange equilibrium constant, and calculate the apparent equilibrium constant at each point.

(c) Check if the apparent equilibrium constant approaches that calculated from the first principles at long time and comment on the result.

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