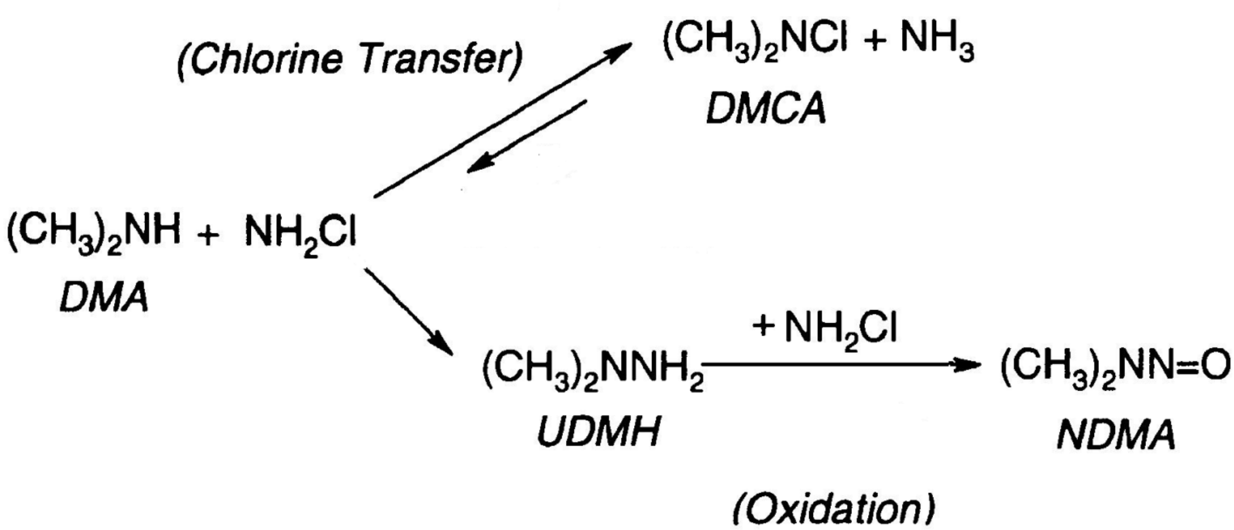
CEE 543 Aut 2012, HW#2

1. *N*-nitrosodimethylamine (NDMA) is a suspected carcinogen that can form via reactions between dimethylamine (DMA) and monochloramine (NH_2Cl). DMA is a precursor for the formation of many industrial chemicals and can enter water supplies as a contaminant in polymers that are used in water treatment. NH_2Cl is frequently generated intentionally in water supplies during water treatment operations, because it can disinfect water without forming chlorinated disinfection byproducts (DBPs). Choi and Valentine (*Water Research*, 36, 817-824 [2002]) suggested that the relevant elementary reactions and the corresponding rate constants are as shown below.



Reaction	Rate constant ($M^{-1}s^{-1}$)
$\mathrm{DMA} + \mathrm{NH_2Cl} \rightarrow \mathrm{DMCA} + \mathrm{NH_3}$	$1.4\text{x}10^{-1}$
$\mathrm{DMA} + \mathrm{NH_2Cl} \leftarrow \mathrm{DMCA} + \mathrm{NH_3}$	$5.83\text{x}10^{-3}$
$\mathrm{DMA} + \mathrm{NH_2Cl} \rightarrow \mathrm{UDMH}$	$1.28\text{x}10^{-3}$
$\mathrm{UDMH} + \mathrm{NH_2Cl} \rightarrow \mathrm{NDMA}$	$1.11\text{x}10^{-1}$

Predict the concentrations of all species that participate in these reactions as a function of time for 500 hours in a batch experiment with initial concentrations of $10^{-5}\,M$ DMA, $10^{-4}\,M$ NH_2Cl, $2\text{x}10^{-5}\,M$ NH_3 and none of the other species shown. Explain the concentrations trends qualitatively.

2. Two reversible, elementary reactions proceed in sequence as follows:

$$2A \rightleftharpoons B + C \rightleftharpoons 2D$$

The rate constants for the reactions are as follows, where '1' and '2' refer to the first and second reaction, respectively, and *f* and *r* designate the forward and reverse reactions.

$$k_{1,f} = 0.04\ \mathrm{M^{-1}s^{-1}} \quad k_{1,r} = 0.01\ \mathrm{M^{-1}s^{-1}} \quad k_{2,f} = 0.10\ \mathrm{M^{-1}s^{-1}} \quad k_{2,r} = 0.10\ \mathrm{M^{-1}s^{-1}}$$

(a) If a solution initially contains 100 mmol/L of A and no B, C, or D, what will the concentrations of A, B, C, and D be at equilibrium?
(b) Repeat part *a* for a solution that initially contains 50 mmol/L each of A and B.
(c) What is the equilibrium constant for the reaction $A \rightleftharpoons D$?

3. On a single plot, sketch curves of chemical energy vs. reaction coordinate for (a) a reaction that releases a large amount of energy but proceeds very slowly, and (b) a reaction that releases a small amount of energy but nevertheless proceeds rapidly.

4. The odor of solutions containing ammonia is generated by volatilization, i.e., transfer into the gas phase, of NH_3 molecules; NH_4^+, like all ions, is essentially non-volatile. The equilibrium constant for Reaction 1 below is $10^{-9.24}$, and the standard Gibbs energy of the volatilization reaction (Reaction 2) is +10.09 kJ/mol.

$$NH_4^+ \rightleftharpoons NH_3(aq) + H^+ \qquad \text{Reaction 1}$$

$$NH_3(aq) \rightleftharpoons NH_3(g) \qquad \text{Reaction 2}$$

A solution containing 10^{-2} *M* total dissolved ammonia species (*TOT*NH_3, the sum of the concentrations of NH_4^+ and NH_3) is at pH 7.25 and 25°C and is in contact with a gas phase containing an NH_3 partial pressure of 10^{-6} atm. Reaction 1 is at equilibrium, but Reaction 2 might not be.

a. Does the chemical driving force favor dissolution of ammonia, volatilization of ammonia, or is the system at equilibrium?

b. How much and in what direction (increase or decrease) would the total Gibbs energy of the system change if 10^{-6} mol of NH_3 was transferred from the gas to solution? You may assume that this transfer is carried out in such a way that the partial pressure of ammonia and the composition of the solution change negligibly.