Problem set on the theory of bimolecular reactions

1. The reaction

$$\mathrm{K_{(g)} + Br_{2(g)} \rightarrow KBr_{(g)} + Br_{(g)}}$$

has an activation energy of zero so that the rate constant is equal to the preexponential factor. At 600 K, the rate constant is approximately $10^{12}\,\mathrm{L\,mol^{-1}s^{-1}}$. Assuming that the reaction occurs at the collision-limited rate, what is the collision cross-section? Determine the radius of a disk with this area. Comment (briefly) on the magnitude of this number.

Note: It may be useful to look up the radii and/or bond lengths of the relevant atoms and molecules for comparison. There are several possible sources for these data (introductory chemistry textbooks, CRC Handbook, some web sites). Happy hunting!

2. Consider the reaction

$$\mathrm{H_{(g)} + CH_{4(g)} \rightarrow H_{2(g)} + CH_{3(g)}}.$$

   (a) The preexponential factor for this reaction is $1.25\times10^{11}\,\mathrm{L\,mol^{-1}s^{-1}}$ over the temperature range 372–1290 K. Estimate the collision efficiency of this reaction given that the radius of a hydrogen atom is 3.7×10^{-11} m and the radius of a methane molecule is about 1.9×10^{-10} m. The molar masses of hydrogen and of carbon atoms are, respectively, 1.0079 and 12.011 g/mol.

   Note: You will have to choose a reasonable temperature for your calculations in this and the following part of this question.

   (b) Calculate the entropy of activation for the reaction. Discuss (briefly) the physical interpretation of the value calculated.

   (c) The activation energy for the reaction is 49.8 kJ/mol. Calculate the activation energy for the reverse reaction given the following data:

Substance	$\Delta \bar{E}_f^\circ$ (kJ/mol)
$CH_{3(g)}$	146.9268
$CH_{4(g)}$	−72.3941
$H_{(g)}$	216.759
$H_{2(g)}$	0

3. Diffusion coefficients for large macromolecules such as antibodies are generally of order $10^{-11}\,\mathrm{m}^2/\mathrm{s}$. Diffusion coefficients for viruses are much smaller, typically about $10^{-12}\,\mathrm{m}^2/\mathrm{s}$. Assuming that the binding of antibodies to viral particles is diffusion-controlled, estimate the rate constant for this process at 25°C. The viscosity of water at this temperature is $8.91 \times 10^{-4}\,\mathrm{Pa\,s}$. Convert your answer to $\mathrm{L\,mol^{-1}s^{-1}}$.