1. Define the terms in and limit to the generality of the Arrhenius expression, \( \ln k = \ln A - \frac{E_a}{RT} \). Include a brief statement on the physical meaning of the terms in the rate expression. Sketch a reaction coordinate for a bimolecular process that is exothermic by 50 kJ/mol, and has \( E_a \) of 15 kJ/mol. The discussion need not be any more than 50-100 words.

See text

2. The rate of formation of C in the reaction 2 A + B \( \rightarrow \) 2 C + 3 D is 1.0 mol dm\(^{-3}\) s\(^{-1}\). State the reaction rate, and the rates of formation or consumption of A, C, and D.

\[
v = \frac{1}{v_j} \frac{d[J]}{dt} = \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{2} \times (1.0 \text{ mol dm}^{-3} \text{ s}^{-1}) = 0.50 \text{ mol dm}^{-3} \text{ s}^{-1}\]  [22.3b].

Rate of formation of D = 3v = \(1.5 \text{ mol dm}^{-3} \text{ s}^{-1}\).

Rate of consumption of A = 2v = \(1.0 \text{ mol dm}^{-3} \text{ s}^{-1}\).

Rate of consumption of B = v = \(0.50 \text{ mol dm}^{-3} \text{ s}^{-1}\).

3, 4. **This problem counts as two problems!** Methane is a by-product of a number of natural processes (such as digestion of cellulose in ruminant animals, anaerobic decomposition of organic waste matter) and industrial processes (such as food production and fossil fuel use). Reaction with the hydroxyl radical OH is the main path by which CH\(_4\) is removed from the lower atmosphere. T. Gierczak, R.K. Talukdar, S.C. Herndon, G.L. Vaghjiani, and A.R. Ravishankara (J. Phys. Chem. A 101, 3125 (1997)) measured the rate constants for the elementary bimolecular gas-phase reaction of methane with the hydroxyl radical over a range of temperatures of importance to atmospheric chemistry. Deduce the Arrhenius parameters \( A \) and \( E_a \) from the following measurements:

<table>
<thead>
<tr>
<th>T/K</th>
<th>206</th>
<th>200</th>
<th>195</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k/10^6 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} )</td>
<td>0.295</td>
<td>0.241</td>
<td>0.217</td>
</tr>
<tr>
<td>( k/10^6 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} )</td>
<td>0.452</td>
<td>0.379</td>
<td>0.295</td>
</tr>
<tr>
<td>( k/10^6 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} )</td>
<td>0.494</td>
<td>0.379</td>
<td>0.295</td>
</tr>
</tbody>
</table>

FYI, Ravishankara works at NOAA here in Boulder, and is an Adjoint member of our Chemistry faculty.

The Arrhenius expression for the rate constant is

\[ k = Ae^{-E_a/RT}\]  [22.31] so \( \ln k = \ln A - \frac{E_a}{RT} \) [22.29].
Using \( \Delta H^\circ \) for the reaction above to estimate the energy difference between reactants and products, sketch the energy profile along the reaction coordinate. Label axes and important places along the reaction path. Within this model, what is the largest value that the rate constant could attain? What is the value of the rate constant at 200 K?

\[
\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{H}
\]

\( \Delta H \sim -62 \text{ kJ/mol}; \) from \( D(\text{H-OH}) = 498 \text{ kJ/mol} \) and \( D(\text{H-CH}_3\text{O}) = 436 \text{ kJ/mol}, \) taken from tables

Reaction cannot be faster than the frequency term \( 8.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \) except that the frequency term can (actually does) have a temperature dependence. But steric factors, etc, make it difficult to make a simple prediction.
5. Suppose we allowed the reaction above to reach equilibrium at 295 K with a measured equilibrium constant $K_{295}$. We then magically found a catalyst that reduced the activation barrier by a factor of two. How would this catalyst change $K_{295}$? Explain.

There is no change in the equilibrium constant. Equilibrium depends only upon initial and final states, not the pathway!