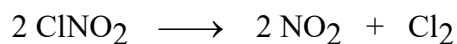
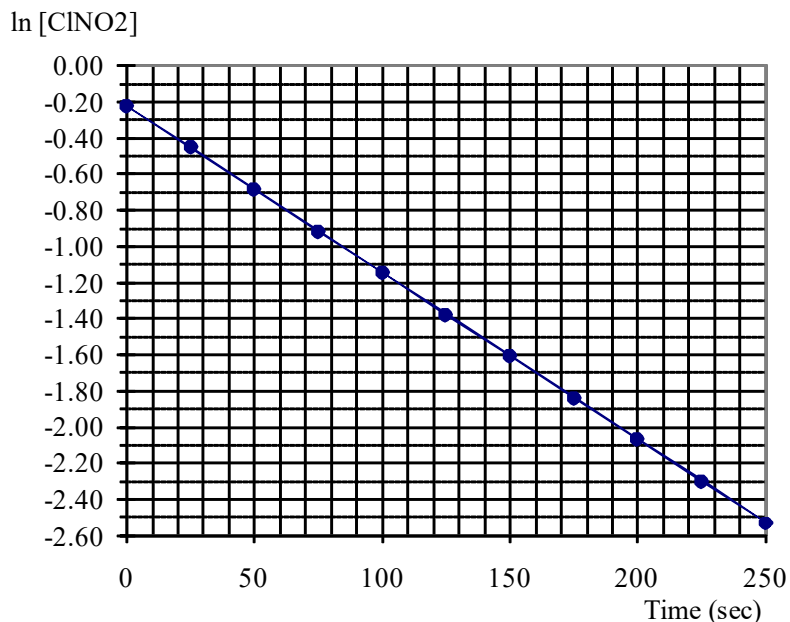


1. In a detailed kinetic study of the following gas-phase reaction, $[\text{ClNO}_2]$ was monitored as a function of time. The experimental data is tabulated and plotted below. Use this information to answer the following questions.



Time (sec)	$[\text{ClNO}_2]$	$\ln[\text{ClNO}_2]$
0	0.800	-0.2231
25	0.635	-0.4542
50	0.504	-0.6852
75	0.400	-0.9163
100	0.317	-1.1473
125	0.252	-1.3784
150	0.200	-1.6094
175	0.159	-1.8405
200	0.126	-2.0715
225	0.100	-2.3026
250	0.079	-2.5336



- (a) (7 points) Write the **rate law** for this reaction. In 25 words or less, explain how you arrived at your answer. (*No calculations are needed here!*)

$$\text{rate} = k[\text{ClNO}_2]$$

Since the plot of $\ln[\text{ClNO}_2]$ vs time is linear, the reaction must be first order. The integrated rate law is shown below in part (d).

- (b) (3 points) The half-life of this reaction is **75 sec**. (*Again, no calculations!*)
- (c) (3 points) **SHOW ALL WORK.** Determine the rate constant (k) of this reaction including proper units.

$$k = \ln 2 / t_{1/2} = \ln 2 / 75 \text{ sec} = 9.24 \times 10^{-3} \text{ sec}^{-1}$$

- (d) (7 points) **SHOW ALL WORK.** Determine the molar concentration of ClNO_2 after the reaction has been in progress for 10.0 min from the start.

$$\begin{aligned} \ln[\text{ClNO}_2]_t &= -kt + \ln[\text{ClNO}_2]_0 \\ &= -(9.24 \times 10^{-3} \text{ sec}^{-1})(600 \text{ sec}) + \ln(0.800) \end{aligned}$$

$$\ln[\text{ClNO}_2]_t = -5.767$$

$$[\text{ClNO}_2]_t = e^{-5.767} = 0.00313 \text{ M}$$

2. (10 points) **SHOW ALL WORK.** The energy of activation of a certain reaction is 145 kJ/mole. Determine the temperature (in °C) at which the rate of this reaction is 1,000 times faster than it is at 25 °C (assuming the same initial concentrations).

$$\ln(k_2/k_1) = -E_a/R [1/T_2 - 1/T_1]$$

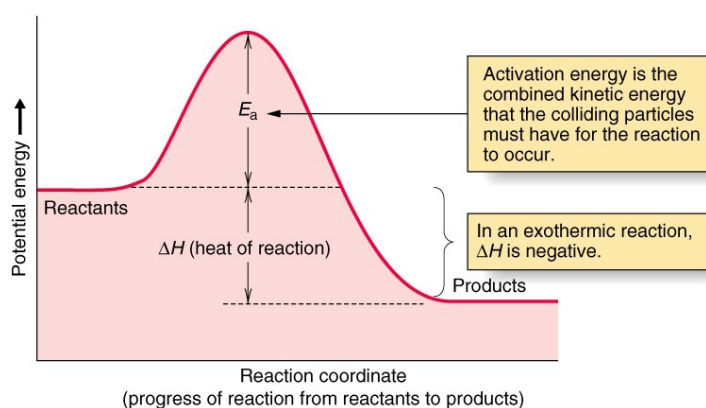
$$\ln(1,000) = -(145 \text{ kJ/mole})/(8.314 \times 10^{-3} \text{ kJ/mole}\cdot\text{K}) (1/T_2 - 1/298 \text{ K})$$

$$6.908 = -(1.744 \times 10^4) (1/T_2 - 3.356 \times 10^{-3})$$

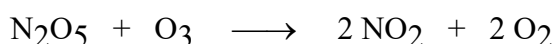
$$1/T_2 - 3.356 \times 10^{-3} = -3.961 \times 10^{-4}$$

$$T_2 = 338 \text{ K} = 65 \text{ }^\circ\text{C}$$

3. (7 points) Sketch and **correctly label** a "reaction coordinate diagram" for an exothermic reaction. Such diagrams are used in the **Transition State** theory of reaction rates.



4. The experimental rate law for the following reaction is found to be: $\text{rate} = k[\text{N}_2\text{O}_5]$.



- (a) (3 points) **In 25 words or less, explain** why this reaction cannot occur by a one-step mechanism.

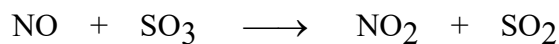
Since the rate does not depend on $[\text{O}_3]$, O_3 cannot be a reactant in the slow step. Therefore more than one step is required.

- (b) (7 points) *Propose* a reasonable **two-step mechanism** for this reaction that is consistent with the experimental rate law. Clearly indicate which step in your mechanism is the rate-determining step. If your proposed mechanism contains an intermediate, circle it.



predicted rate law (based on slow step): $\text{rate} = k[\text{N}_2\text{O}_5]$

5. A kinetic study of the following gas-phase reaction gave the concentration vs initial rate data summarized below.



Expt	[NO]	[SO ₃]	initial rate (mole/L·sec)
(1)	0.150	0.250	1.65×10^{-4}
(2)	0.450	0.450	5.35×10^{-4}
(3)	0.150	1.350	4.81×10^{-3}
(4)	0.150	0.450	5.35×10^{-4}

- (a) (10 points) Determine the **rate law** for this reaction. **Clearly SHOW how you arrive at your answer.**

Expts 1 and 3 (constant NO):

$$\{[\text{SO}_3]_3 / [\text{SO}_3]_1\}^x = \text{rate}_3 / \text{rate}_1$$

$$(1.35 / 0.25)^x = (4.81 \times 10^{-3}) / (1.65 \times 10^{-4})$$

$$5.4^x = 29.15 \quad \therefore x = 2 \quad (\text{2nd order in SO}_3)$$

Expts 2 and 4 (constant SO₃):

$$\{[\text{NO}]_2 / [\text{NO}]_4\}^y = \text{rate}_2 / \text{rate}_4$$

$$(0.450 / 0.150)^y = (5.35 \times 10^{-4}) / (5.35 \times 10^{-4})$$

$$3^y = 1 \quad \therefore y = 0 \quad (\text{zero order in NO})$$

$$\text{rate} = k [\text{SO}_3]^2$$

- (b) (4 points) Determine the value for the **rate constant** (k) for the above reaction. **SHOW ALL WORK (including proper units).**

$$k = \text{rate} / [\text{SO}_3]^2 = (1.65 \times 10^{-4} \text{ mole} / \text{L}\cdot\text{sec}) / (0.250 \text{ mole} / \text{L})^2$$

$$k = 2.64 \times 10^{-3} \text{ L} / \text{mole}\cdot\text{sec} \quad (\text{or } \text{M}^{-1} \text{ sec}^{-1})$$

6. (8 points) **SHOW ALL WORK.** For a certain reaction, $\Delta H^\circ = -95.2 \text{ kJ}$ and $\Delta S^\circ = -157 \text{ J/K}$. Determine ΔS_{surr} and ΔS_{univ} (in J/K) for this reaction at 850 K. *Based on these results*, is the reaction spontaneous at this temperature? *Explain briefly* (but do not exceed the allotted space!).

The reaction is exothermic, releasing heat which increases the entropy of the surroundings.

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}} / T = -(-95,200 \text{ J}) / (850 \text{ K}) = +112 \text{ J/K}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -157 \text{ J/K} + 112 \text{ J/K} = -45 \text{ J/K}$$

The reaction is NOT spontaneous because the total entropy of the universe would decrease which is contrary to the second Law of Thermodynamics.

7. (3 points) For a chemical system in a state of dynamic equilibrium, ΔH is equal to which of the following? Circle any that apply.

$\Delta S/R$ E_{cell} $\log Q$ $\Delta E/n$ ΔG $T\Delta S$ $-RT\ln K$

8. (8 points) **SHOW ALL WORK.** An 80.0-L volume of an ideal gas in a cylinder with a piston is at a pressure of 3.0 atm. While the system is held at constant temperature, enough weight is placed on the piston to increase the external pressure to 10.0 atm. For the resulting process, determine q (heat) and w (work) in units of kJ, and with proper signs. (*Note:* 1 L·atm = 101.3 J)

$$P_1V_1 = P_2V_2 \quad (3.0 \text{ atm})(80.0 \text{ L}) = (10.0 \text{ atm})V_2$$

$$V_2 = 24 \text{ L}$$

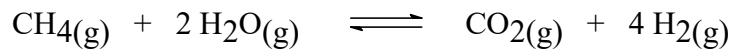
$$w = -P\Delta V = -(10.0 \text{ atm})(24 \text{ L} - 80 \text{ L}) = +560 \text{ L}\cdot\text{atm} \quad (\text{work is done on system})$$

$$w = (560 \text{ L}\cdot\text{atm})(0.1013 \text{ kJ} / \text{L}\cdot\text{atm}) = 57 \text{ kJ}$$

$$\Delta E = q + w = 0 \quad (\text{since } T \text{ is constant, } \Delta E = 0 \text{ for an ideal gas})$$

$$q = -w = -57 \text{ kJ} \quad (\text{system loses heat to surroundings})$$

9. In a potential hydrogen-based economy, one possible source of hydrogen would be the oxidation of natural gas with steam at high-temperature as in the following reaction. Some relevant thermodynamic data is also tabulated below.



Compound	ΔH°_f (kJ/mole)	S° (J/mole·K)
$\text{CH}_4(\text{g})$	- 75	186
$\text{H}_2\text{O}(\text{g})$	- 242	189
$\text{CO}_2(\text{g})$	- 394	214
$\text{H}_2(\text{g})$	0	131

- (a) (10 points) **SHOW ALL WORK.** Determine whether this reaction is spontaneous at 25 °C by calculating the appropriate thermodynamic quantity.

$$\Delta H^\circ = (-394) + 4(0) - [(-75) + 2(-242)] = 165 \text{ kJ}$$

$$\Delta S^\circ = 214 + 4(131) - [186 + 2(189)] = 174 \text{ J/K} = 0.174 \text{ kJ/K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 165 \text{ kJ} - (298 \text{ K})(0.174 \text{ kJ/K}) = +113 \text{ kJ}$$

Positive ΔG indicates that the reaction is NOT spontaneous at 25 °C.

- (b) (10 points) **SHOW ALL WORK.** Calculate the temperature (in °C) at which the equilibrium constant (K) for this reaction is equal to 100.

$$\Delta G = \Delta H^\circ - T\Delta S^\circ = -RT \ln K \quad (\text{assuming that } \Delta H^\circ \text{ and } \Delta S^\circ \text{ are temp independent})$$

$$\text{rearranging: } T = \Delta H / (\Delta S - R \ln K)$$

$$T = (165 \text{ kJ}) / [(0.174 \text{ kJ/K} - (8.314 \times 10^{-3} \text{ kJ/K}) \ln(100))] = 1216 \text{ K}$$

$$T = 1,216 - 273 = 943 \text{ }^\circ\text{C}$$