Unit 4, Lesson 04: Reaction Mechanisms Answers to Homework

1. The following equations represent the elementary steps in a reaction mechanism. The overall reaction is exothermic.

Step 1:	$P + \cancel{T}$	$\rightarrow$	$\cancel{PT}$	fast, exothermic
Step 2:	$\cancel{PT} + Q_2$	$\rightarrow$	$PQ + \cancel{TQ}$	slow, endothermic
Step 3:	$\cancel{TQ} + P$	$\rightarrow$	$PQ + \cancel{T}$	fast, exothermic

a) Overall: $2\,P + Q_2 \rightarrow 2\,PQ$

b) Reaction intermediates are substances that are formed in one step and then consumed in a later step. For this reaction, PT and TQ are reaction intermediates. "T" is NOT a reaction intermediate because it is consumed early in the reaction and later reformed (it is a catalyst).

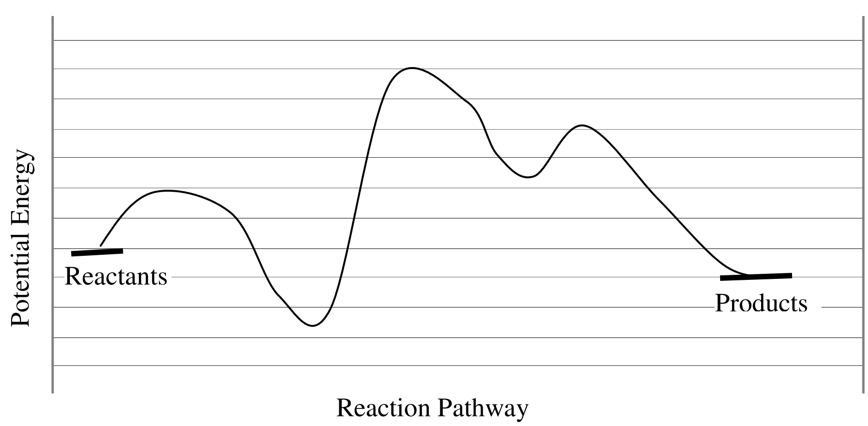
c) The rate-determining step for this reaction is the slow step, step 2.

d) Which would produce a greater increase in the overall rate of the reaction: increasing the concentration of P or increasing the concentration of Q_2 ? Explain.

The overall reaction can only go as fast as the slowest step.

To increase the rate of reaction, the concentration of the reactants involved in the rate-determining step must be increased. Q_2 is involved in the RDS, so increasing its concentration will increase the overall rate of the reaction. Increasing P will have no effect on the overall rate because it is involved in steps 1 and 3, which are already fast and do not affect the overall rate.

e) Sketch an approximate potential energy diagram (energy profile) for the reaction.



We do not know whether the overall reaction is endothermic or exothermic, so you could draw either. The important features of the graph are that steps 1 and 3 have small activation energies (little "humps") and are exothermic, while step 2 must have a large activation energy (big "hump") and be endothermic.

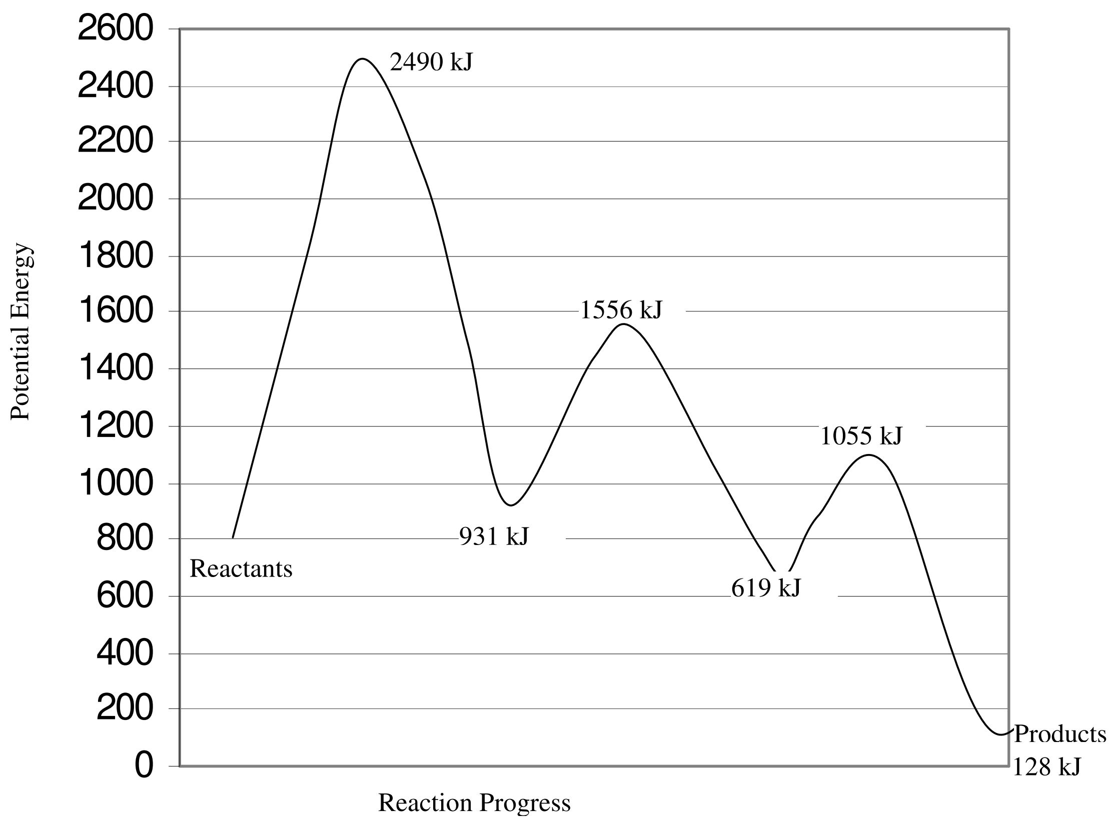
4. Consider these three reactions as the elementary steps in the mechanism for a chemical reaction.

(i)	$H_{2(g)} + NO_{(g)} \rightarrow H_2O_{(g)} + \cancel{N}_{(g)}$	$E_a = 1690$ kJ	$\Delta H = +131$ kJ
(ii)	$\cancel{N}_{(g)} + NO_{(g)} \rightarrow N_{2(g)} + \cancel{O}_{(g)}$	$E_a = 625$ kJ	$\Delta H = -312$ kJ
(iii)	$\cancel{O}_{(g)} + H_{2(g)} \rightarrow H_2O_{(g)}$	$E_a = 436$ kJ	$\Delta H = -491$ kJ

a) Overall: $2\ H_{2(g)} + 2\ NO_{(g)} \rightarrow 2\ H_2O_{(g)} + N_{2\ (g)}$ $\Delta H = -672$ kJ

b) ΔH for the overall reaction is $\Delta H = -672$ kJ (Hess's Law)

c) Draw, with an appropriate scale, the potential energy diagram (energy profile) for the reaction.



d) The rate-determining step is the step with the highest E_a, which is step (i).

e) What is E_a for the overall reaction? You must calculate this from the potential energy diagram.

The overall E_a for the reaction must be calculated from the potential energy diagram; it is the difference in energy from the original reactants (800 kJ) to the top of the highest bump (2490 kJ). The overall E_a is therefore 1690 kJ, or E_a for the first step.

f) Suggest why the activation energy for the first step is larger than for the other two steps.

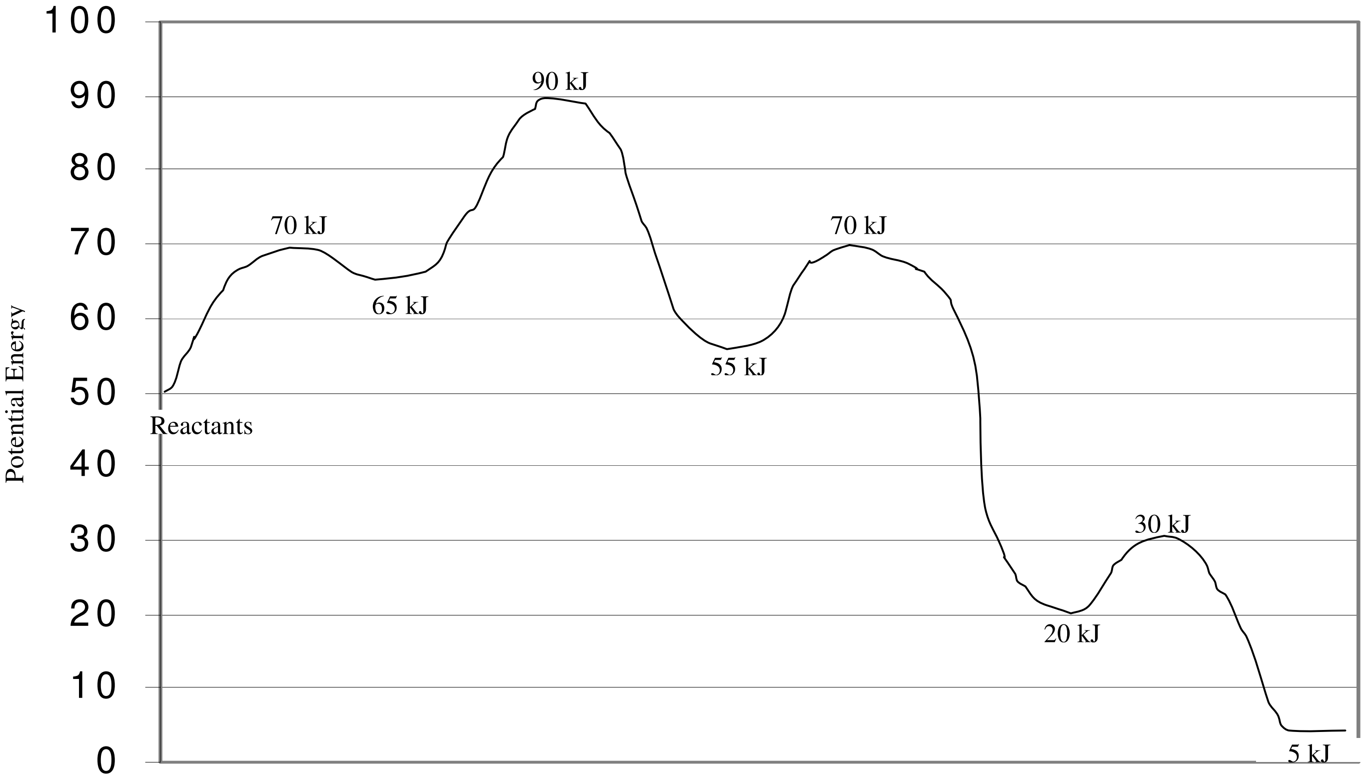
The first step involves breaking apart H_2 and NO molecules. Both of these molecules are stable, so they will require considerable energy to break apart which gives this step a high E_a value. The second and third steps involve species that are single atoms. No bonds must be broken in order for these species to react, so they will require lower activation energies.

5. The following are steps in a reaction mechanism:

(i)	$X_2 \rightarrow$ ~~X~~ $+$ ~~X~~	$E_a = 20$ kJ	$\Delta H = +15$ kJ
(ii)	~~X~~ $+ YH_4 \rightarrow$ ~~YH_3~~ $+ HX$	$E_a = 25$ kJ	$\Delta H = -10$ kJ
(iii)	~~YH_3~~ $+$ ~~X_2~~ $\rightarrow YH_3X +$ ~~X~~	$E_a = 15$ kJ	$\Delta H = -35$ kJ
(iv)	~~X~~ $+$ ~~X~~ $\rightarrow$ ~~X_2~~	$E_a = 10$ kJ	$\Delta H = -15$ kJ

a) Overall: $X_2 + YH_4 \rightarrow HX + YH_3X$ $\Delta H = -45$ kJ

c) Draw, with an appropriate scale, the potential energy diagram (energy profile) for the reaction. Assume that the potential energy of the reactants is 50 kJ.



d) The rate-determining step is step 2 because it has the highest E_a.

e) The E_a for the overall reaction is 40 kJ (from the original reactants at 50 kJ to the top of the second hump at 90 kJ).