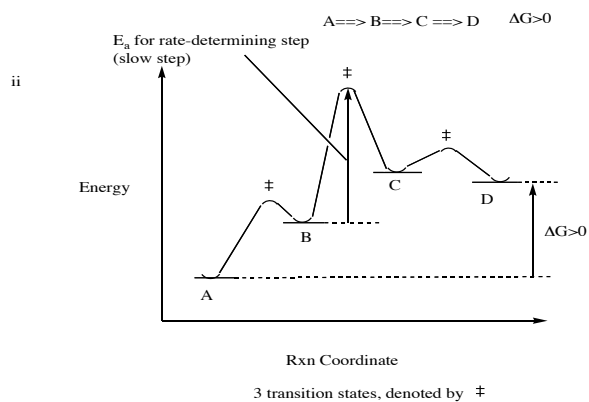
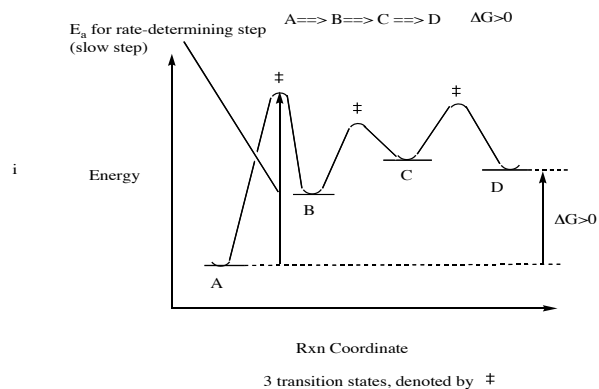
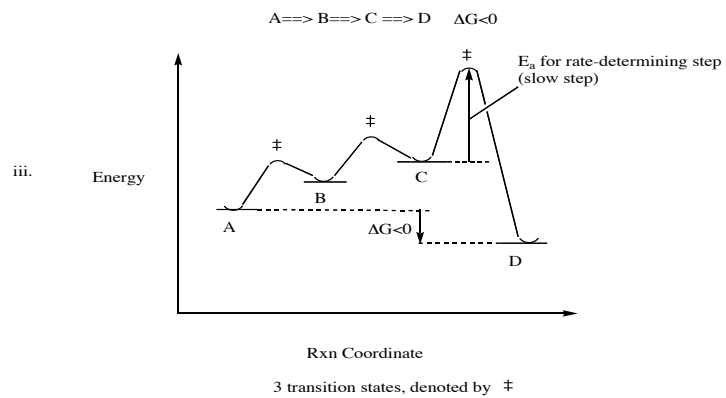
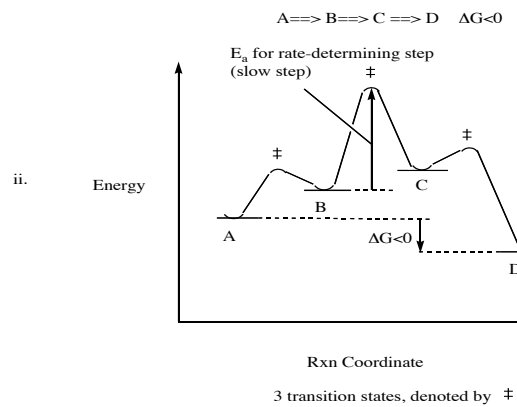
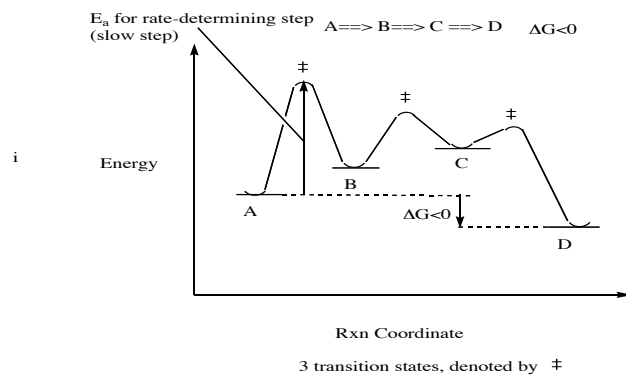
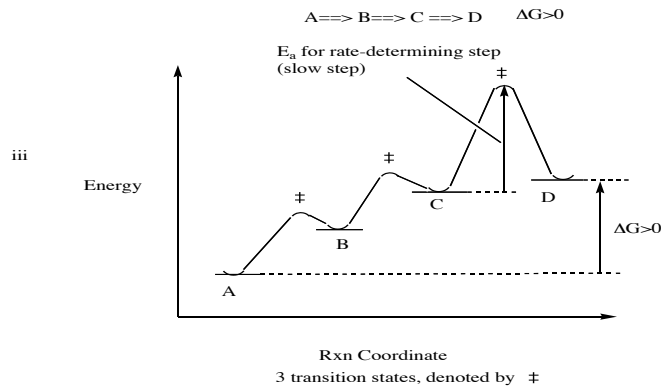


Additional Problems for practice:

1. Draw a reaction energy diagram (graph of potential energy versus reaction coordinate) for a three-step endothermic reaction with the
  - (a) first step rate-determining
  - (b) the second step rate-determining
  - (c) the third step rate determining

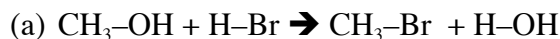
Do the same (a-c) for a three step exothermic reaction. For each graph, indicate  $\Delta G$  for the reaction (is it positive or negative?). How many transition states are there? Label them.



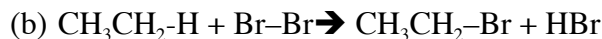


2. Use the information in table 4-2 to calculate  $\Delta H^\circ$  for these reactions:

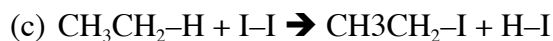
$$\Delta H^\circ_{\text{rxn}} = \Sigma \text{BDE bonds broken} - \Sigma \text{BDE bonds formed}$$



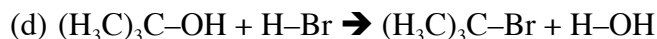
$$\Delta H^\circ_{\text{rxn}} = 91 \text{ kcal/mol} + 88 \text{ kcal/mol} - 70 \text{ kcal/mol} - 119 \text{ kcal/mol} = -10 \text{ kcal/mol}$$



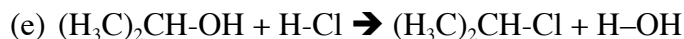
$$\Delta H^\circ_{\text{rxn}} = 98 \text{ kcal/mol} + 46 \text{ kcal/mol} - 68 \text{ kcal/mol} - 88 \text{ kcal/mol} = -12 \text{ kcal/mol}$$



$$\Delta H^\circ_{\text{rxn}} = 98 \text{ kcal/mol} + 36 \text{ kcal/mol} - 53 \text{ kcal/mol} - 71 \text{ kcal/mol} = 10 \text{ kcal/mol}$$



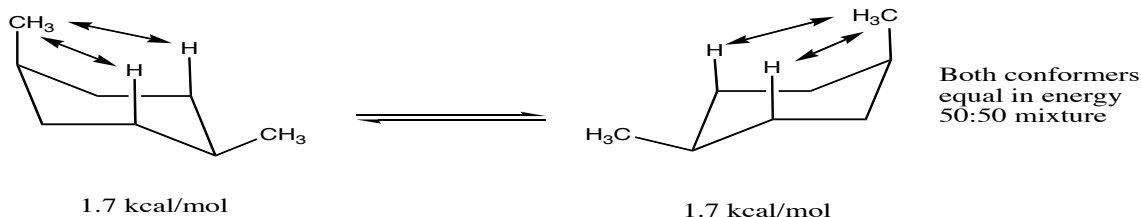
$$\Delta H^\circ_{\text{rxn}} = 91 \text{ kcal/mol} + 88 \text{ kcal/mol} - 65 \text{ kcal/mol} - 119 \text{ kcal/mol} = -5 \text{ kcal/mol}$$



$$\Delta H^\circ_{\text{rxn}} = 91 \text{ kcal/mol} + 103 \text{ kcal/mol} - 80 \text{ kcal/mol} - 119 \text{ kcal/mol} = -5 \text{ kcal/mol}$$

3. Draw the two possible conformations of *cis*-1,4-dimethylcyclohexane. Denote all 1,3-diaxial interactions for both conformations. Calculate the total strain energy for each conformation. Circle the more stable conformation. Finally, determine the ratio of the two conformations at equilibrium (use the relation between Gibbs free energy and the equilibrium constant). Repeat the exercise for *trans*-1,4-dimethylcyclohexane.

*cis*-1,4-dimethylcyclohexane



*trans*-1,4-dimethylcyclohexane

