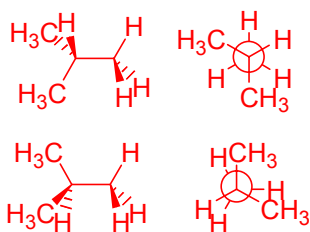
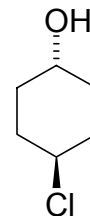
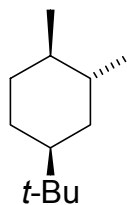
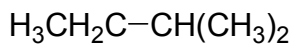
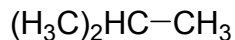


CHEM211 Problem Set
Reaction Energetics

1) For the molecules below:

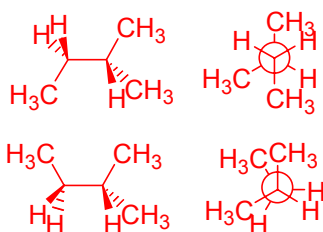
- Draw the most stable and least stable conformations.
- Calculate the difference in energy between the conformations.
- Calculate the equilibrium constant (K_{eq}) for conversion between the conformations at room temperature (70 °F, 21 °C, 294 K).



$$4 + 6 + 6 = 16 \text{ kJ/mol}$$

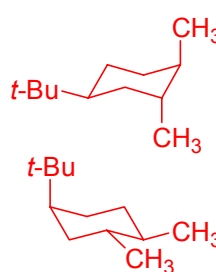
$$\Delta G^\circ = -RT \ln K_{eq}$$

$$K_{eq} = 1.4 \times 10^{-3}$$



$$11 - 4 = 7 \text{ kJ/mol}$$

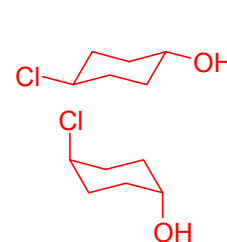
$$K_{eq} = 5.7 \times 10^{-2}$$



$$2 \times (11.4) - 4 \times (3.8)$$

$$= 7.6 \text{ kJ/mol}$$

$$K_{eq} = 4.46 \times 10^{-2}$$



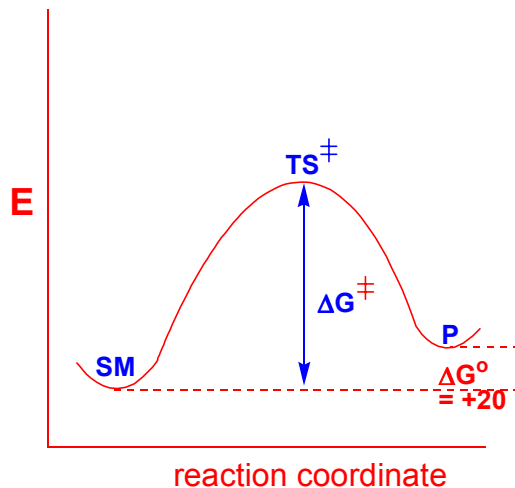
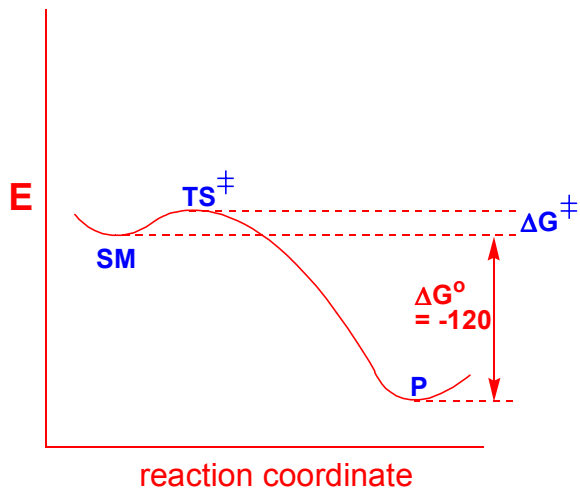
$$2 \times (1.0) + 2 \times (2.1)$$

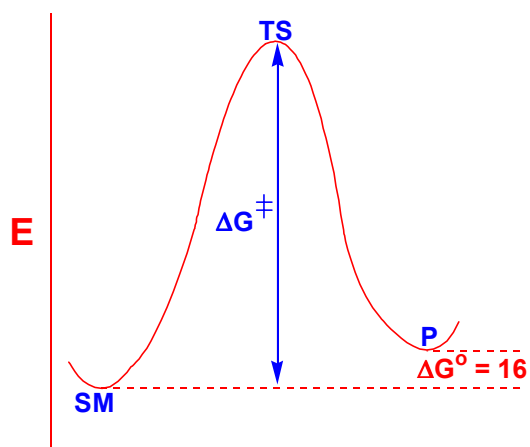
$$= 6.2 \text{ kJ/mol}$$

$$K_{eq} = 7.92 \times 10^{-2}$$

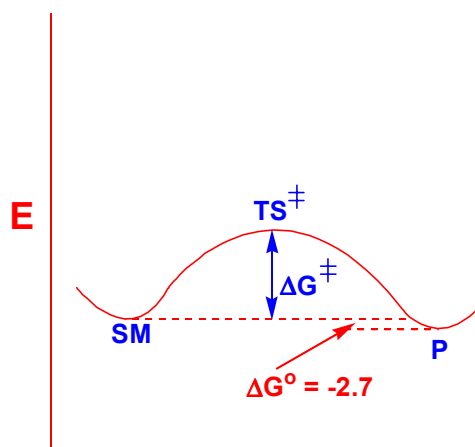
2) Sketch an energy diagram to match each of the following descriptions:

- Fast reaction; $\Delta G^\circ = -120 \text{ kJ/mol}$.
- Slow reaction; $\Delta G^\circ = 20 \text{ kJ/mol}$.
- Very slow reaction; $K_{eq} = 1.36 \times 10^{-3}$.
- Fast reaction; $K_{eq} = 3.0$.
- A two step reaction; first step is fast; second step is slow; $\Delta G^\circ = -80 \text{ kJ/mol}$.
- $\Delta G_1^\ddagger = 200 \text{ kJ/mol}$; $\Delta G_2^\ddagger = 50 \text{ kJ/mol}$; $\Delta G^\circ = -40 \text{ kJ/mol}$.

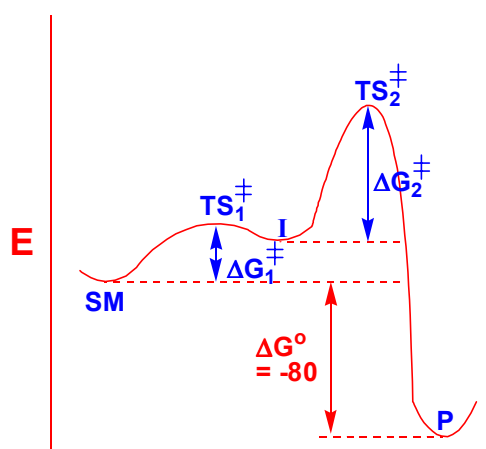




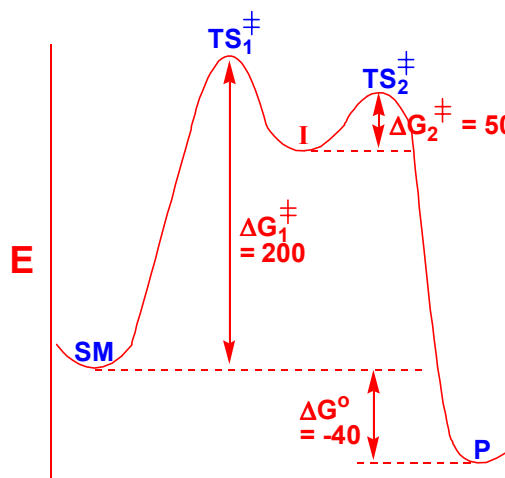
reaction coordinate



reaction coordinate



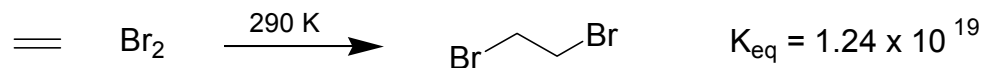
reaction coordinate



reaction coordinate

3) For each energy diagram in (2), label starting material(s) (SM), product(s) (P), intermediate(s) (I), transition state(s) (TS[‡]), activation energy(s) (ΔG[‡]) and free energy (ΔG[°]).

4) For the reactions below, calculate ΔG[°], ΔH[°] and ΔS[°].



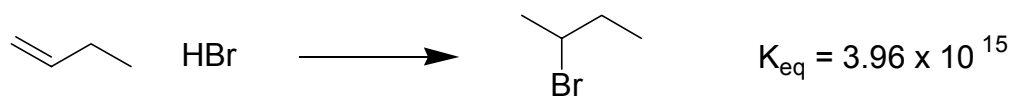
$$\Delta G^\circ = -RT \ln K_{\text{eq}} = -(8.315 \text{ J/K mol})(290\text{K}) \ln (1.24 \times 10^{19}) = -106,000 \text{ J/mol} = -106 \text{ kJ/mol}$$

$$\Delta H^\circ = \Delta H_{\text{f bonds broken}} - \Delta H_{\text{f bonds formed}} = \Delta H_{\text{f C=C}} + \Delta H_{\text{f Br-Br}} - 2(\Delta H_{\text{f C-Br}}) - \Delta H_{\text{f C-C}} =$$

$$611 + 193 - 2(285) - 376 = -142 \text{ kJ/mol}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S^\circ = -(\Delta G^\circ - \Delta H^\circ)/T = -(-106 - (-142))/290 = -0.124 \text{ kJ/K mol} = -124 \text{ J/K mol}$$



$$\Delta G^\circ = -RT \ln K_{\text{eq}} = -(8.315 \text{ J/K mol})(290\text{K}) \ln (3.96 \times 10^{15}) = -87,000 \text{ J/mol} = -87 \text{ kJ/mol}$$

$$\Delta H^\circ = \Delta H_{\text{fC=C}} + \Delta H_{\text{fH-Br}} - \Delta H_{\text{fC-H}} - \Delta H_{\text{fC-Br}} - \Delta H_{\text{fC-C}} =$$

$$611 + 366 - 420 - 285 - 376 = -104 \text{ kJ/mol}$$

$$\Delta S^\circ = -(\Delta G^\circ - \Delta H^\circ)/T = -(-87 - (-104))/290 = -0.060 \text{ kJ/K mol} = -60 \text{ J/K mol}$$



$$\Delta G^\circ = -RT \ln K_{\text{eq}} = -(8.315 \text{ J/K mol})(290\text{K}) \ln (0.13) = 4900 \text{ J/mol} = 4.9 \text{ kJ/mol}$$

$$\Delta H^\circ = \Delta H_{\text{fC-H}} + \Delta H_{\text{fC-Br}} + \Delta H_{\text{fC-C}} - \Delta H_{\text{fO-H}} - \Delta H_{\text{fC=C}} =$$

$$420 + 285 + 376 - 437 - 611 = 33 \text{ kJ/mol}$$

$$\Delta S^\circ = -(\Delta G^\circ - \Delta H^\circ)/T = -(4.9 - 33)/290 = 0.097 \text{ kJ/K mol} = 97 \text{ J/K mol}$$