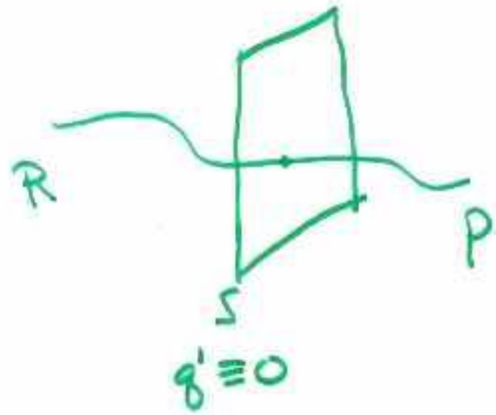
Transition State Theory (pp 46-48)



$$k = \int_S \dot{q}_1 \, \chi_r \, e^{-\beta H} \frac{dp_1}{Qh} \prod_{i=2}^{n} \frac{dq_i dp_i}{h}$$

$\chi_r \to$ TST: 1 if $\dot{q}_1 > 0$, 0 otherwise

Now let H be <u>separable</u>

$$H = H^0(p_1) + H^*(q_1, q_2 p_2 \cdots q_n p_n)$$

Hamiton's eq says: $\dot{q}_1 = (\partial H^0 / \partial p_1)$

$$k_{TST} = \int_{-\infty}^{\infty} \prod_{i=2}^{n} \frac{dq_i dp_i}{h} e^{-\beta H^*} \int_0^{\infty} dp_1 \underbrace{\left[\frac{\partial H^0}{\partial p_1}\right] e^{-\beta H^0}}_{-kT\left[\frac{\partial e^{-\beta H^0}}{\partial p_1}\right]} \Big/ Qh$$

$$= \left(\frac{kT}{h}\right) \frac{1}{Q} \int \prod_{i=2}^{n} \frac{\partial p_i \partial q_i}{h} e^{-\beta H^*}$$

$$\boxed{k_{TST} = \left[\frac{kT}{h}\right]\left[\frac{Q^*}{Q}\right] = \left(\frac{kT}{h}\right) e^{-\Delta G^* / kT}}$$