Problem 7.10

7.10 What are the major differences between the $F + H_2 \rightarrow FH + H$ and $F + C_2H_4 \rightarrow C_2H_3F + H$ potential energy surfaces?

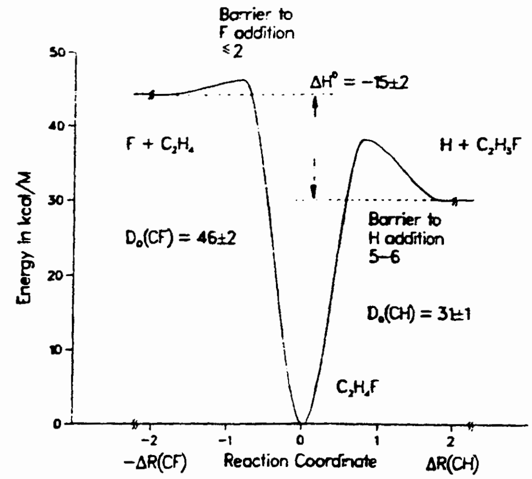
Potential Energy Surfaces

$$\left\{\begin{array}{l} F + H_2 \longrightarrow FH + H \\ F + C_2H_4 \longrightarrow FC_2H_3 + H \end{array}\right.$$

From "Ab Initio Molecular Orbital Studies of $C_2H_4 + H$ and $F + C_2H_4$". H.B. Schlegel, K.C. Bhalla and W.L. Hase, J. Phys. Chem. 1982, 86, 4883–4888, and Physical chemistry, I.N. Levine, we can illustrate the potential energy surfaces of both of the reactions above. (next page)

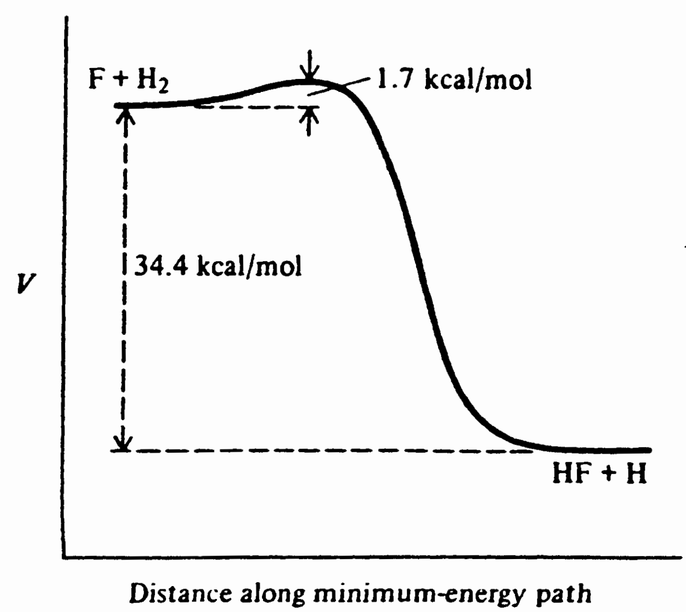
Both of the reactions present a small barrier to addition of F ($\leq$ 2 kcal/mol), but the major difference between these two reactions is the fact that the transition state for C_2H_4 + F is trapped in a deep well and there is a barrier to H addition about 5–6 kcal/mol, whereas there is no well for H_2 + F reaction.

The Journal of Physical Chemistry, Vol. 86, No. 25, 1982



Best estimates for the reaction of fluorine with ethylene. The relative energies were obtained by combining experimental data with reliable theoretical energy differences and including zero-point energy.

Potential energy profile for the collinear FH_2 system. [Adapted from I. N. Levine, *Physical Chemistry* (McGraw-Hill, New York, 1988). Reproduced with permission of McGraw-Hill.]



Problem 7.12

7.12 What is the mathematical property common to both minima and saddlepoints on potential energy surfaces?

Potential Energy surface

$V(q_1, \ldots, q_n)$ where $(q_i)_{i \in [1,n]}$ are n independent variables (modes) that completely define the surface.

Minima and Saddle-points of energy surface are both extrema. The mathematical property associated with extrema on a surface is:

$$\forall i \in [1,n] \quad \left(\frac{\partial V}{\partial q_i}\right)_{extremum} = 0 .$$

Chapter 8. Molecular Collision Dynamics

8.1

Consider the following "single beam" experiment, which enables the total cross section for elastic scattering to be measured directly. A beam of molecules of species B at a high translational energy E is passed through a gas of species G which is at very low pressures; E is sufficiently large that the atoms of G are essentially stationary with respect to B. Let the velocity of B be v.

(a) From the definition of the cross section, show that the total number of deflections (collisions) of B per unit time per G atom is $\sigma n_B v$, where n_B is the density of B and σ is the total elastic cross section for B–G collisions. (Assume that only elastic collisions are possible.)

(b) Show that the total number of B–G collisions per unit time in a volume V is $\sigma V v n_B n_G$, where n_G is the density of G.

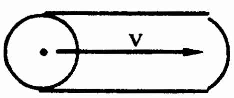
(c) Suppose that the volume in question has (constant) area A and length dx. Suppose also that the intensity of B is J = (density of B) $\cdot\, v$ and is initially $J = J_0 = n_B v$. Show that the change in intensity over dx is $dJ = -J\sigma n_G\, dx$.

(d) Show that the overall change in intensity over a finite distance x is given by

$$\ln (J_0/J) = n_G \sigma X$$

It is plain that the measurement of this intensity change enables the total cross section to be determined from one experiment (see also chapter 9, problem 1.)

a.



, volume = σv

σ = cross-section

total # of deflections of B per unit time per G atom is density of B X volume

$$= n_B \sigma v$$

b. # of G atoms $= n_G V$

$V =$ volume

n_G = density of G atoms $= \dfrac{\text{number of G atoms}}{V}$

total # B/G collision per unit time = $(\sigma n_B V) n_G V$

c. $V = A \cdot dx$

Intensity of B = J = (density of B) $\cdot$ V = $\dfrac{\#B}{\text{Area}}$

$J_o = n_B V$

$\Delta J = J_{final} - J_G$

= # of collisions final - # collision initial and

$$\Delta J = \frac{\#\ \text{scattering collisions}}{\text{Area}}$$

$$= d\frac{(-n_B n_G \sigma v V)}{A} = - \frac{n_G V \sigma J}{A} = - J n_G \sigma dx$$

x is only paramter that can change

so $\underline{dJ = - J\sigma\, nG\, dx}$

d. $$- \int_{J_o}^{J} \frac{dJ}{J} = \sigma \quad n_G \int_{o}^{x} dx$$

$$- \ln (J/J_o) = n_G \sigma x$$

$$\ln (J_o/J) = n_G \sigma x$$

8.2 Gas viscosity is given by

$$\eta = \frac{5\pi}{32\sqrt{2}} \frac{\mu \bar{v}}{Q}$$

[R. D. Present, *Kinetic Theory of Gases*, New York: McGraw-Hill, 1958], where the average velocity $\bar{v} = (8k_B T/\pi\mu)^{1/2}$, μ is the collision-reduced mass, and

$$Q = \frac{1}{32}\left(\frac{\mu}{2k_B T}\right)^4 \int_0^\infty dv \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin^3\theta \, I(\theta) \, v^7 \exp\left(-\frac{\mu v^2}{4k_B T}\right) dv$$

Given that the differential cross section of a hard sphere of diameter d is $I(\theta) = d^2/4$, find the viscosity of a gas of hard spheres.

Gas viscosity is given by

$$\eta = \frac{5\pi}{32\sqrt{2}} \cdot \frac{\mu \bar{v}}{Q}$$

where
$$\begin{cases} \bar{v} = \sqrt{\dfrac{8kT}{\pi\mu}} & \text{is the average velocity} \\ \mu & \text{is the reduced mass} \\ Q = \dfrac{1}{32}\left(\dfrac{\mu}{2kT}\right)^4 \displaystyle\int_0^\infty\int_0^\pi\int_0^{2\pi} \sin^3\theta . I(\theta) . v^7 \exp\left(\dfrac{-\mu v^2}{4kT}\right) dv \, d\theta \, d\varphi \end{cases}$$

The differential cross section of a hard sphere of diameter d is given by

$$I(\theta) = \frac{d^2}{4}$$

Let us compute the viscosity of a gas of hard spheres.

$$Q = \frac{1}{32}\left(\frac{\mu}{2kT}\right)^4 \int_0^{2\pi} d\varphi \, . \int_0^{\pi} I(\theta)\sin^3\theta \, d\theta \, . \int_0^{\infty} v^7 \exp\left(-\frac{\mu v^2}{4kT}\right) dv$$

$$\int_0^{2\pi} d\varphi = [\varphi]_0^{2\pi} = 2\pi$$

$$\int_0^{\pi} I(\theta)\sin^3\theta \, d\theta = \frac{d^2}{4}\int_0^{\pi} \sin^3\theta \, d\theta$$

$$= \frac{d^2}{4}\int_0^{\pi} (1-\cos^2\theta)\sin\theta \, d\theta .$$

$$= \frac{d^2}{4}\left[\int_0^{\pi} \sin\theta \, d\theta - \int_0^{\pi} \cos^2\theta . \sin\theta \, d\theta \right]$$

$$= \frac{d^2}{4}\left[[-\cos\theta]_0^{\pi} + \left[\frac{\cos^3\theta}{3}\right]_0^{\pi} \right]$$

$$= \frac{d^2}{4}\left[\frac{\cos^3\theta}{3} - \cos\theta\right]_0^{\pi}$$

$$= \frac{d^2}{4}\left[\frac{(-1)^3}{3} - (-1) - \left(\frac{1}{3} - 1\right)\right]$$

$$= \frac{d^2}{4} \times \frac{4}{3} = \frac{d^2}{3}$$

$$\int_0^{\infty} v^7 \exp\left(-\frac{\mu v^2}{4kT}\right) dv = \left(\frac{4kT}{\mu}\right)^4 \int_0^{\infty} x^7 \exp(-x^2)\, dx$$

where $x = \left(\frac{\mu}{4kT}\right)^{1/2} v .$

We can derive by successive integration by parts that :

$$\int x^7 e^{-x^2} dx = P_7(x)\, e^{-x^2}$$

where P is a polynomial of degree at most 7.

and $$\frac{d}{dx}\left(P_7(x) e^{-x^2} \right) = x^7 e^{-x^2}$$

Let $P_7(x) = \sum_{n=0}^{7} a_n x^n$

Then we obtain

$$\frac{d}{dx}\left(P_7(x)\, e^{-x^2} \right) = -2x\, P_7(x)\, e^{-x^2} + e^{-x^2} \sum_{n=1}^{7} a_n . n . x^{n-1}$$

$$\begin{aligned} = e^{-x^2} \Big[& 7a_7 x^6 + 6a_6 x^5 + 5a_5 x^4 + 4a_4 x^3 \\ & + 3a_3 x^2 + 2a_2 x + a_1 - 2a_7 x^8 \\ & - 2a_6 x^7 - 2a_5 x^6 - 2a_4 x^5 - 2a_3 x^4 \\ & - 2a_2 x^3 - 2a_1 x^2 - 2a_0 x \Big] \end{aligned}$$

$$\begin{aligned} = e^{-x^2} \Big[& (-2a_7) x^8 + (-2a_6) x^7 + (7a_7 - 2a_5) x^6 \\ & + (6a_6 - 2a_4) x^5 + (5a_5 - 2a_3) x^4 \\ & + (4a_4 - 2a_2) x^3 + (3a_3 - 2a_1) x^2 \\ & + (2a_2 - 2a_0) x + a_1 \Big] \end{aligned}$$

$$= e^{-x^2} \times x^7$$

$$\begin{cases} -2a_7 = 0 \\ -2a_6 = 1 \\ 7a_7 - 2a_5 = 0 \\ 6a_6 - 2a_4 = 0 \\ 5a_5 - 2a_3 = 0 \\ 4a_4 - 2a_2 = 0 \\ 3a_3 - 2a_1 = 0 \\ 2a_2 - 2a_0 = 0 \\ a_1 = 0 \end{cases}$$

$$a_7 = a_1 = 0$$

$$a_6 = -1/2 .$$

$$a_5 = 0$$

$$a_3 = 0$$

$$a_1 = 0$$

$$a_4 = 3a_6 = -3/2$$

$$a_2 = 2a_4 = -3$$

$$2a_0 = 2a_2 \Leftrightarrow a_0 = a_2 = -3$$

$$P_7(x) = -1/2\, x^6 - 3/2\, x^4 - 3x^2 - 3$$

$\boxed{8.3}$ Show that Hamilton's equations of motion

$$-\frac{\partial H}{\partial q_i} = \frac{dp_i}{dt} \qquad \frac{\partial H}{\partial p_i} = \frac{dq_i}{dt}$$

with $H(q_i, p_i) = \Sigma_i\,(p_i^2/2\mu_i) + V(q_1, \ldots, q_N)$ are equivalent to Newton's law

$$\frac{d^2 q_i}{dt^2} = -\frac{\partial V}{\partial q_i}$$

We want to show that Hamiltonian's equations of motion are equivalent to Newton's law.

Hamiltonian's equations of motion.

Let a system described by coordinates q_i and momenta $\dot{q}_i$

where $\dot{q}_i = \frac{dq_i}{dt}$

We assume the Potential energy depends only on position of the particles of the system, so, $V(q_i)$ is a function of the only q_i, whereas the kinetic energy $K(\dot{q}_i)$ is a function of the momenta $\dot{q}_i$ ($K = \Sigma\, \frac{1}{2}\mu_i\, \dot{q}_i$ usually.)

The Lagrangian is defined by

$$L(q_i, \dot{q}_i) = K(\dot{q}_i) - V(q_i)$$

$$dH = \Sigma \dot{q}_i \, dp_i - \Sigma \left(\frac{\partial L}{\partial q_i} \right) dq_i$$

From equations of Lagrange

$$\left(\frac{\partial L}{\partial q_i} \right) = \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) = \frac{d}{dt} (p_i) = \dot{p}_i$$

hence $\quad dH = \Sigma \dot{q}_i \, dp_i - \Sigma \dot{p}_i \, dq_i .$

$$= \Sigma \left(\frac{\partial H}{\partial p_i} \right) dp_i + \Sigma \left(\frac{\partial H}{\partial q_i} \right) dq_i .$$

Therefore, we obtain Hamiltonian's equations of motion :

$$\boxed{\left(\frac{\partial H}{\partial p_i} \right) = \dot{q}_i \qquad \left(\frac{\partial H}{\partial q_i} \right) = - \dot{p}_i}$$

Since we use Newton's Law to achieve these equations of motions, it is obvious that these laws are equivalent.

Nevertheless, Let us show this equivalence.

Given the Hamiltonian

$$H(p_i, q_i) = \sum \frac{p_i^2}{2\mu_i} + V(q_i)$$

$K(p_i) = \sum \frac{p_i^2}{2\mu_i}$ is the Kinetic Energy.

$$\frac{\partial H}{\partial p_i} = \dot{q}_i = \frac{dq_i}{dt}$$

$$\frac{\partial H}{\partial p_i} = \frac{\partial K}{\partial p_i} = \frac{p_i}{\mu_i} = \frac{dq_i}{dt}$$

so $p_i = \mu_i \frac{dq_i}{dt}$

which is the known analogous to $\vec{p} = m\vec{v}$ in the generalized Hamiltonian approach.

$$\frac{\partial H}{\partial q_i} = -\dot{p}_i = -\frac{dp_i}{dt}$$

$$\left\{ \begin{array}{l} \dfrac{\partial H}{\partial q_i} = \dfrac{\partial V}{\partial q_i} \\ \dfrac{dp_i}{dt} = \dfrac{d}{dt}\left(\mu_i \dfrac{dq_i}{dt}\right) = \mu_i \dfrac{d^2 q_i}{dt^2} \end{array} \right.$$

hence $$\boxed{\mu_i \frac{d^2 q_i}{dt^2} = - \frac{\partial V}{\partial q_i}}$$

From Hamiltonian's equations of motion, we can then derive Newton's law $\vec{F} = m\vec{a}$, where the Force $\vec{F}$ is a gradient of potential energy, and the acceleration $\vec{a}$ is the second time derivative of the corresponding coordinate:

$$\begin{cases} \mu_i \dfrac{d^2 q_i}{dt^2} = - \dfrac{\partial V}{\partial q_i} \\ m \; \vec{a} = \vec{F} \end{cases}$$

Using mass_weighted cartesian coordinates

$$\bar{q}_i = \sqrt{\mu_i}\, q_i$$

$$\begin{cases} \dfrac{d^2 \bar{q}_i}{dt^2} = \sqrt{\mu_i} \dfrac{d^2 q_i}{dt^2} \\ \dfrac{\partial V}{\partial \bar{q}_i} = \dfrac{1}{\sqrt{\mu_i}} \dfrac{\partial V}{\partial q_i} \end{cases}$$

$$\mu_i \frac{d^2 q_i}{dt^2} = - \frac{\partial V}{\partial q_i} \Leftrightarrow \sqrt{\mu_i} \frac{d^2 q_i}{dt^2} = \frac{-1}{\sqrt{\mu_i}} \frac{\partial V}{\partial q_i} \Leftrightarrow \boxed{\frac{d^2 \bar{q}_i}{dt^2} = - \frac{\partial V}{\partial \bar{q}_i}}$$