Problems and solutions for Chapter 3

P.A. The exoergicity of the reaction is defined as the change in energy between the ground state of the reactants and that of the products. Why is the $H + D_2(v = 0) \rightarrow D + HD$ just a shade endoergic? Much of our understanding of isotope effects on reactivity stems from the considerations you will make in solving this problem.

A. ΔE_0 , the exoergicity of the reaction is the difference between the ground state energy of the products and the ground state energy of the reactants, see figure 1.1. In purely classical mechanics the reaction will have $\Delta E_0 = 0$ because the potential energy curve of D₂ and of HD are the same⁺. But the ground state energies of D₂ and of HD are not quite equal because of the different zero point energy of the vibration. To simplify the discussion we take the potentials for small displacements to be harmonic and the mass of the D atom to be twice that of H. The harmonic frequency is $\sqrt{k_e/\mu}$ where the force constant k_e is invariant for the different isotopomers. The reduced mass of D₂ is twice that of H₂ so its zero point energy is $1/\sqrt{2}$ that of H₂. The reduced mass of HD is 4/3that of H₂ so the ZPE of HD is $\sqrt{3}/2$ that of the vibrational quantum of H₂. The reaction is a shade endoergic, $\Delta E_0 \cong (\sqrt{3} - \sqrt{2})/2$ the vibrational quantum of H₂.

P.C. One sometimes loosely writes $k(T) = \langle v \sigma_R(v) \rangle \approx \langle v \rangle \langle \sigma_R(v) \rangle$ where the brackets denote an average over a thermal velocity distribution. The exact result, equation (3.8),

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⁺ Strictly speaking, the two potentials are the same only in the Born-Oppenheimer approximation.

shows that this is really not so. To correctly factor out the mean (relative) velocity out of the thermal rate constant we can proceed as follows. One can define not just the number density of molecules with velocity in a given range. It is also possible to determine the flux density of molecules with velocity in a given range. (a) Show that the flux density gives a somewhat higher weight to faster molecules and then (b) verify the comment after equation (3.8). Historically, the velocity distribution of molecules was measured (by O. Stern, 1911) in a setup similar in principle to figure 2.1 with a velocity selector but without any scattering cell. The raw experimental results did not fit the Boltzmann distribution. Einstein then pointed out that what the experiment measures is the flux density and not the number density. All fell into place but we still sometimes fail to distinguish between a number and a flux density.

S.C. Refer to equation (3.7). The number density of molecules with a speed in the range v to v+dv is, at thermal equilibrium, f(v)dv where f(v) is the Maxwell-Boltzmann density function $4\pi v^2 \exp(-\mu v^2/2k_{\rm B}T)/N$ where $N = (2\pi k_{\rm B}T/\mu)^{3/2}$ insures that the density is normalized, $\int_0^\infty f(v)dv = 1$. The flux density is the fraction of molecules with flux in a given range. Since, cf. Equation (2.1), the flux is the velocity times the number density, the flux density is proportional to vf(v) with a proportionality constant determined by normalization. The most probable speed is $\sqrt{2k_{\rm B}T/\mu}$ for the number density and $\sqrt{3k_{\rm B}T/\mu}$ for the flux density showing, as is only to be expected, that the flux density gives more weight to faster moving molecules.

P.E. The entropy of activation. If, as is quite often the case, the reaction requires some restrictions on how the reactants come together, then the entropy of the reactive reactants should be lower than that of the reactants. You could then say that there is an entropic barrier to reaction. By examining the temperature dependence of the activation energy,

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equation (3.9), you can come up with a rigorous expression for the entropy of activation. Do so. Later we shall recognize that there can be situations where entropic considerations act in the opposite direction and favor the reaction. (This is most common for unimolecular elimination or dissociation processes). Can you suggest an example where the reactive reactants will be less constrained than the reactants?

S.E. Thermodynamic⁺ shows that at thermal equilibrium when we are given F(T), the Helmholtz free energy as a function of temperature, we can compute the mean energy by the (Gibbs-Helmholtz) equation

$$\langle E \rangle = -k_B T^2 \frac{\partial}{\partial T} \left(\frac{F(T)}{k_B T} \right)$$

It follows from the definition of the Arrhenius activation energy by equation (3.3) that we can write the rate constant in a 'thermodynamic form'

$$k(T) = A \exp\left(-\frac{F_{\rm a}}{k_{\rm B}T}\right)$$

where the exponent is the free energy of activation rather than simply the energy of activation E_a . The energy of activation can still be written and evaluated as the slope of the Arrhenius plot of $\ln k(T)$ vs. 1/T

$$E_{\rm a} = k_{\rm B}T^2 \frac{\partial \ln k(T)}{\partial T} = -k_{\rm B}T^2 \frac{\partial}{\partial T} \left(\frac{F_{\rm a}(T)}{k_{\rm B}T}\right)$$

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⁺ We offer a thermodynamic approach. A stat mech formulation can be found in R. D. Levine, *J. Phys. Chem.* **83**, 159 (1979).

By comparing with the Tolman definition of the activation energy, equation (3.9), we identify the free energy of activation $F_a(T)$ as the difference between the free energy of the reactive reactants and the free energy of the reactants. The entropy of activation S_a is read from the usual expression for the Helmholtz free energy

$$F_{\rm a}(T) = E_{\rm a}(T) - T S_{\rm a}(T)$$

so that an equivalent thermodynamic form is

$$k(T) = A \exp\left(\frac{S_{a}}{k_{B}}\right) \exp\left(-\frac{E_{a}}{k_{B}T}\right)$$

If the activation energy is nearly temperature independent so is the entropy of activation and we can put the Arrhenius pre-exponential factor to equal $A \exp(S_a/k_B)$. In general both the activation energy and entropy vary with temperature and these two variations are not independent but are related by the Clausius form

$$\partial S_{\rm a} / \partial T = T^{-1} \partial E_{\rm a} / \partial T$$

that can also be written in the Gibbs-Helmholtz form

$$S_{\rm a} = -\frac{\partial F_{\rm a}}{\partial T}$$

The entropy of activation favors reaction whenever the reactive reactants are less constrained than all the reactants. For most bimolecular reactions the opposite is the case, as reaction requires partial or complete freezing of degrees of freedom of the separated and non interacting reactants, see chapter 6, section 6.1.4.1 in particular.

P.G. The Tolman expression for the activation energy. The derivation of the Tolman result for the activation energy as the difference between the mean energy of the reactive reactants and the mean energy of all reactants, equation (3.9), was for the special case that there was only translational energy. In appendix 3.A we showed how to express the

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reaction rate constant as an average of contributions from different internal states of the reactants. Show that in this more general case we have

$$E_a \equiv \langle E_T + E_{Internal} \rangle_{\text{reactive reactants}} - \langle E_T + E_{Internal} \rangle_{\text{all reactants}}$$

S.G. The rule 'average over states of the reactants' means that the thermal reaction rate constant can be written as

$$k(T) = \sum_i p_i(T) k_i(T)$$

Here *i* sums over the internal states of the reactants, $p_i(T)$ is the fraction of reactants in the state *i* at thermal equilibrium and $k_i(T)$ is the reaction rate constant for state-selected reactants. $k_i(T)$ is temperature dependent because of the collision energy dependence of the cross section for reaction for reactants in the state *i*. For $k_i(T)$ we have the Tolman result

$$E_{\rm a}^{(i)} = k_{\rm B}T^2 \frac{\partial \ln k_i(T)}{\partial T} = \langle E_{\rm T} \rangle$$
 reactive reactants for $-\langle E_{\rm T} \rangle$ reactants in state i

where the mean translational energy of the reactants, $3k_{\rm B}T/2$ is independent of their internal state.

The first contribution to the overall activation energy is then $\sum_i p_i(T)E_a^{(i)}$. There is a second contribution due to the temperature dependence of the Boltzmann factors $p_i(T) = \exp(-E_i/k_{\rm B}T)/Q(T)$. The partition function Q(T), appendix 6A, is the sum over states, so that the mean internal energy is, equation (6.A.7), $k_{\rm B}T^2 \partial \ln Q / \partial T$. The second contribution to the overall activation energy is

$$k_{\rm B}T^2 \frac{\sum_i k_i(T) \frac{\partial}{\partial T} p_i(T)}{\sum_i k_i(T) p_i(T)} = \frac{\sum_i k_i(T) E_i p_i(T)}{\sum_i k_i(T) p_i(T)} - \left\langle E_{\rm I} \right\rangle_{\rm reactants} = \left\langle E_{\rm I} \right\rangle_{\rm reactants} - \left\langle E_{\rm I} \right\rangle_{\rm reactants}$$

where E_{I} is the internal energy.

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P.*I. The harpoon mechanism for excited states. Excited electronic states have a lower I.P.'s and so are generally more likely to react by a harpoon mechanism. But the lowest I.P.'s are for excited electronic states of the alkali metals. (a) The first excited state of Na is about 2.1 eV and of K about 1.56 eV above the ground state. How will the reaction cross section in the table above change if these atoms are used as reagents? (b) Why stop at the first excited state? How will the reaction cross section change if higher excited state atoms are used as reagents? Experimental answer: the reaction cross section will not continue to grow indefinitely, Bersohn (1976). Why not? Hint: look at the value of the crossing radius. For more insight see section 9.3.2.

S.I. (a). The excited states of the alkali atoms have even lower ionization potentials than the ground state atoms. Therefore the energy required to transfer an electron to a halogen molecule is lower and the crossing radius R_x , equation (3.18), is even larger. The estimated reaction cross section, πR_x^2 , is consequently expected to be higher than for ground state atoms. (b). The expectation expressed in (a) can fail if the crossing radius R_x becomes so large that the charge fails to transfer from the alkali atom to the halogen molecule even though it is energetically possible. In section 9.3.3 we relate the probability of charge transfer to a so-called energy gap at R_x . Empirically, the energy gap decreases exponentially as R_x increases.

P.K. Steric factor for ion-molecule reactions. Purpose: to compute the cone of acceptance for reaction, section 3.2.8.1, for the model discussed in problem H. When the molecule is not spherical, e.g., H₂, the long range potential depends not only on the ion-molecule distance but also on the orientation angle, γ , between the axis of the molecule and the ionmolecule distance *R*, see equation (2.18). (a) For a non polar molecule we can take this into account by allowing the polarizability of the molecule to be different along its axis

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and perpendicular to it. Using the second Legendre polynomial, a convenient functional representation is $V(R,\gamma) \xrightarrow{\log \operatorname{range}} -(C/R^4)(1+aP_2(\cos\gamma))$. *a* is the asymmetry parameter and $C = e^2\alpha/2$ for a singly charged ion. If you have access to a suitable program, plot the potential on a polar grid where *R* is the radius and γ is the angle. If not, plot the potential vs. *R* for $\gamma=0$ and 90° . (b) Determine the maximal impact parameter for which reaction is allowed as a function of the approach angle γ . (c) If the molecule is polar, e.g., HCl, it will have a dipole moment. Then the leading terms in the long range potential are $V(R,\gamma) \xrightarrow{\log \operatorname{range}} -(C/R^4) - e\mu\cos\gamma/R^2$. For this case too, determine the maximal impact parameter for which reaction is allowed as a function is allowed as a function of the approach angle γ . For this case too, determine the maximal impact parameter for which reaction is allowed as a function is allowed as a function of the approach angle of the approach angle γ . For this case too, determine the maximal impact parameter for which reaction is allowed as a function of the approach angle γ . In the general case, one should also allow for the asymmetry of the R^{-4} term and for the polarization of the ion by the dipole, which gives rise to a R^{-6} term.

S.K. (b). The determination of the impact parameter for which reaction between an ion and a molecule is possible proceeds as in section 3.2.5.1 except that the strength parameter *C*, equation (3.25), is now dependent on the angle of approach γ . We provide the details for the case (c) when the molecule has a dipole. (c) The long range effective potential is

$$V_{\rm eff}(R) \xrightarrow{\rm long range} - \frac{C}{R^4} - \frac{e\mu\cos\gamma}{R^2} + \frac{E_{\rm T}b^2}{R^2}$$

The location of the barrier in the effective potential is at the root of equation (3.22)

$$\frac{\partial}{\partial R} V_{\text{eff}}(R) \bigg|_{R=R_{\text{max}}} = \frac{4C}{R_{\text{max}}^5} + \frac{2e\mu\cos\gamma}{R_{\text{max}}^3} - \frac{2E_{\text{T}}b^2}{R_{\text{max}}^3} = 0 \Longrightarrow \frac{4C}{R_{\text{max}}^2} = 2(E_{\text{T}}b^2 - e\mu\cos\gamma)$$

The height of the barrier is

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$$V_{\rm eff}(R_{\rm max}) = -\frac{(E_{\rm T}b^2 - e\mu\cos\gamma)^2}{4C} - \frac{(E_{\rm T}b^2 - e\mu\cos\gamma)e\mu\cos\gamma}{2C} + \frac{(E_{\rm T}b^2 - e\mu\cos\gamma)E_{\rm T}b^2}{2C}$$
$$= \frac{(E_{\rm T}b^2 - e\mu\cos\gamma)^2}{4C}$$

Reaction is possible for such values of the impact parameter *b* when $E_T \ge V_{eff}(R_{max})$ or for the range of impact parameters limited as

$$b^2 \le \sqrt{\frac{4C}{E_{\rm T}}} + \frac{e\mu\cos\gamma}{E_{\rm T}}$$

The range of impact parameters that lead to reaction is seen to be strongly dependent on the angle of approach but the effect diminishes the higher is the collision energy.

P. O. Laser assisted recombination. The problem is to compute the cross section for forming a bound species during the collision^{*}. The key consideration is that the colliding Hg atoms, as described in figure 3.B.1, will absorb light when they are at a distance R_x apart. This is the distance when the electronic energy separation between the ground and excited states equals the energy of the laser photon. Say that all collisions absorb light. (a) Show that the cross section for formation of the bound excited state is $\pi R_x^2(1-V_g(R_x)/E_T)$. (b) Plot this cross section vs. the collision energy and show that it is monotonically decreasing, being largest for very slow collisions. (c) Argue that your

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^{*} Ordinarily, when two atoms collide they will not recombine to form a stable bound diatomic. Rather, they will emerge as two unbound atoms. This is so even when their potential is attractive and has a deep well corresponding to a stable diatomic. The reason is that the total energy needs to be conserved. In the region where the potential energy is attractive the kinetic energy increases so as to keep the sum constant. To form a bound state we need some mechanism for removing the energy from the pair of atoms. Typically this is done by a third body that takes the excess energy away. Following Gross and Dantus (1997), appendix 3.B suggests that we can do something else: use a laser to form a bound, electronically excited, stable molecule.

result in (a) also provides a small correction for the cross section of harpoon reactions. [See P. Gross and M. Dantus, *J. Chem. Phys.* **106**, 8013 (1997), Dantus (2001) and J. Kohel and J. W. Keto, *J. Chem. Phys.* **113**, 10551 (2000) and references therein for examples of laser assisted reactions].

S.O. (a). Reaction is assumed to occur when the reactants can reach the distance R_x while moving under an attractive potential V(R). The distance R_x is determined by the special conditions of the problem like a crossing from a weakly attractive covalent potential to a strongly attractive ionic one as in a harpoon mechanism or it is the ('Condon', see section 7.0.1) distance at which an absorption of a photon takes place as in appendix 3.B and figure B3.1. The condition for the classical turning point being to the left of R_x defines the maximal impact parameter that leads to reaction

$$E_{\rm T} \left(1 - \frac{b^2}{R_{\rm x}^2} \right) - V(R_{\rm x}) \ge 0 \quad \text{or } b_{\rm max}^2 = R_{\rm x}^2 \left(1 - \frac{V(R_{\rm x})}{E_{\rm T}} \right) = R_{\rm x}^2 \left(1 + \frac{|V(R_{\rm x})|}{E_{\rm T}} \right)$$

The potential V(R) is attractive so $V(R_x) < 0$. The cross section is therefore <u>decreasing</u> with increasing collision energy. (c) For the harpoon mechanism the potential V(R) is the weakly attractive long range potential between the covalent reactants. At the large value of the crossing radius $V(R_x)$ is small so the correction to the estimate πR_x^2 for the cross section is small except at very low collision energies.

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