Problem and solutions for Chapter 1

P.A. The rare gas ion Ar^+ reacts with H_2 to form ArH^+ . The reaction is excergic. Provide one physical model why the nascent product will be vibrationally excited. To continue with this reaction go to problem B and then to C. The F+H₂ reaction also leads to nascent HF molecules that are vibrationally excited. What chemical argument can be used to make this observation further support the model?

S. A. The spectator model applied to the momentum of the Ar^+ ion implies that the molecule ArH^+ moves at the same velocity after the collision as did the Ar^+ ion before the collision. Energy released by the reaction must therefore be preferentially channeled into the vibration of the ArH^+ molecular ion. We expect that considerable energy is released because the chemistry of the very electronegative Ar^+ ion must be similar to that of the neutral F atom. Indeed the F+H₂ system is isoelectronic with Ar^++H_2 . The ArH^+ molecular ion is therefore expected to be strongly bound with a well depth comparable to that of HF. For a more in depth discussion see B. H. Mahan, J. Chem. Phys. **55**, 1436 (1971), Acc. Chem. Res. **8**, 55 (1975).

P.B. Spectator stripping: a quantitative version of section 1.2.2. It is easy to control and to measure the velocity of an ion. Say we study the final (relative) kinetic energy of ArH^++H as a function of the initial (relative) kinetic energy of Ar^+ and H_2 . Argue that spectator behavior, equation (1.1), implies that roughly one half of the initial kinetic energy appears as products' translation. In the general A+BC case you should get that with the A atom as the spectator the final (primed) kinetic energy is related to the initial one as

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$$E_T' = \left(m_{\rm A}m_{\rm C} / (m_{\rm A} + m_{\rm B})(m_{\rm B} + m_{\rm C})\right)E_T$$

S.B. * By using the notation of appendix 5.B it is possible to solve an even more general problem. See also the solution of problem G below. Let Q'_1 be a mass-scaled coordinate in the direction R' along which the products recede from one another. We chosse the mass scaling, see appendix 5.B such that the final kinetic energy of relative motion can be written as $E'_T = \frac{1}{2}\dot{Q}'_T$. We leave it to show that $Q'_1 = -\cos\beta Q_1 + \sin\beta Q_2$. Then, if no forces acted and since Q_1 and Q_2 are orthogonal directions

$$E'_{T} = \frac{1}{2}\dot{Q}_{1}^{\prime 2} = \cos^{2}\beta \frac{1}{2}\dot{Q}_{1}^{2} + \sin^{2}\beta \frac{1}{2}\dot{Q}_{2}^{2}$$
$$= \cos^{2}\beta E_{T} + \sin^{2}\beta E_{vib}$$

From the definition of the skew angle β , the first term is the result that is to be shown. The second term shows the fraction of reagent vibrational excitation that is converted to kinetic energy of the receding products. To get more help and more physical insight go to page 405.

P.C. As in problems A and B but now let us give the incident Ar^+ ion even higher initial kinetic energies and detect the products. Beyond a certain energy, not too high, there is a steep drop in the formation of ArH^+ , [K. M. Ervin and P. B. Armentrout, *J. Chem. Phys.* **83**, 166 (1985)]. Why? What is happening to the product ion? The bond energy of H₂ is about 435 kJmol⁻¹. That of ArH^+ is about 370 kJmol⁻¹. (a) What is the exo(or endo)ergicdity of the of reaction of Ar^+ and H₂? (b) Estimate the energy at which formation of bound ArH^+ drops off.

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S.C. ArH⁺ dissociates to Ar+H⁺ so, as discussed by Mahan, see above, the ground state of the products correlates with the Ar+H₂⁺electronic state of the reactants and not with the entrance channel Ar⁺+H₂. To compute the exoergicity of the reaction Ar⁺+H₂ \rightarrow ArH⁺+H we need the difference in ionization potentials of Ar and H or, equivalently, the bond dissociation energy of ArH⁺ to Ar⁺+H. This energy is about 6 eV. Since the bond dissociation energy of H₂ is about 4.48 eV, the reaction is exoergic by about 1.52 eV. From A or B, about 50% of the initial kinetic energy ends up NOT as translational energy of ArH⁺ is about 3.86 eV. The initial kinetic energy at which the ArH⁺ product is predicted to be formed with more energy than needed for dissociation is therefore $2 \cdot (3.86 - 1.52) = 4.68 \text{eV}$. For the experimental results see figure 3.2 and also problem 3.J. The paper by Ervin and Armentrout offers additional discussion.

P.*G. The unaffected bond is a spectator. In the A+BCD \rightarrow AB+CD reaction it is often the case that the vibrational energy of CD is hardly changed during the reaction. Why? Make a structural model as follows. (a) Introduce coordinates that allow you to write the kinetic energy as a sum of uncoupled terms. For the reactants these can be the C-D distance, the distance of B to the center of mass of CD and the distance of A to the center of mass of ABC. Express the kinetic energy in these coordinates. See D. W. Jepsen and J. O. Hirschfelder, *Proc. Nat'l. Acad. Sci. US* **45**, 249 (1959). (b) For the products the coordinates can be the C-D and A-B distances and the distance from the center of mass of AB to the center of mass of CD. Express the kinetic energy in these coordinates. (c) Next, examine the kinetic energy of C-D motion and show that it is uncoupled to the other motions and is unaffected by the rearrangement. Where is the approximation? It is that kinetic energy is not necessarily conserved if there are forces acting. In chapter 10 we will call the above 'a *kinematic model*'.

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S.*G. The kinetic energy of a four-atom A+BCD system is a sum of four uncoupled terms,

$$T = \frac{1}{2}m_{\rm A}\dot{R}_{\rm A}^2 + \frac{1}{2}m_{\rm B}\dot{R}_{\rm B}^2 + \frac{1}{2}m_{\rm C}\dot{R}_{\rm C}^2 + \frac{1}{2}m_{\rm D}\dot{R}_{\rm D}^2$$

where \dot{R}_X is the velocity of atom X. This simple form has two drawbacks, it includes, implicitly, the kinetic energy of the motion of the center of mass of the A+BCD system and the coordinates used are not those of direct interest to a chemist. We want to exhibit the kinetic energy of the motion of the center of mass because no forces are acting on it so this kinetic energy is conserved during the collision. Also, as chemists we would rather center attention on bond distances. This is particularly so in the present problem where we want to show that the energy of the CD bond is expected not to change during the reaction. Writing the kinetic energy in a convenient form is a topic that will occupy us all the way to chapter 10. As a first step let us begin with a three atom system and then simplify the problem by making the atoms move on a line, say the X axis. Then introduce the two relative coordinates, one set for the reactants and one for the products



$$x_1 = \frac{m_{\rm B} x_{\rm B} + m_{\rm C} x_{\rm C}}{m_{\rm B} + m_{\rm C}} - x_{\rm A} \quad , \quad x_2 = x_{\rm C} - x_{\rm B}$$

$$z_1 = \frac{m_A x_A + m_B x_B}{m_A + m_B} - x_C$$
, $z_2 = x_B - x_A$

The transformation between the two sets of coordinates is

$$\begin{pmatrix} z_1 \\ z_2 \end{pmatrix} = \begin{pmatrix} -m_A & -m_B M \\ m_A + m_B & (m_A + m_B)(m_B + m_C) \\ 1 & -m_C \\ 1 & m_B + m_C \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} , \quad M = m_A + m_B + m_C$$

The kinetic energy of the three atom system is written as the sum of the kinetic energy of the center of mass plus the kinetic energy of the internal system (without any cross terms)

$$T = \frac{1}{2}m_{\rm A}\dot{x}_{\rm A}^2 + \frac{1}{2}m_{\rm B}\dot{x}_{\rm B}^2 + \frac{1}{2}m_{\rm C}\dot{x}_{\rm C}^2$$
$$= \frac{1}{2}M\dot{X}^2 + \frac{1}{2}\mu_{\rm A-BC}\dot{x}_{\rm I}^2 + \frac{1}{2}\mu_{\rm BC}\dot{x}_{\rm 2}^2$$

$$MX = m_{\rm A}x_{\rm A} + m_{\rm B}x_{\rm B} + m_{\rm C}x_{\rm C}$$

$$\mu_{\text{A-BC}} = \frac{m_{\text{A}}m_{\text{BC}}}{M} \quad , \quad \mu_{\text{BC}} = \frac{m_{\text{B}}m_{\text{B}}}{m_{\text{BC}}}$$

In chapter 5 we will rewrite the internal kinetic energy as

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$$T = \frac{\mu}{2} \left(\dot{Q}_1^2 + \dot{Q}_2^2 \right)$$
$$Q_1 \equiv x_1/a \quad , \quad Q_2 \equiv ax_2$$

where

$$\frac{\mu}{a^2} = \mu_{A-BC} = \frac{m_A m_{BC}}{M} \text{ and } \mu a^2 = \mu_{BC} = \frac{m_B m_C}{m_{BC}}$$
$$\mu^2 = \mu_{A-BC} \mu_{BC} = \frac{m_A m_B m_C}{M}$$

For the A+BCD \rightarrow AB+CD reaction we can chose the two sets of internal coordinates as follows. The first set consists of the coordinate of atom A relative to the center of mass of BCD

$$x_{1} = \frac{m_{\rm B}x_{\rm B} + m_{\rm C}x_{\rm C} + m_{\rm D}x_{\rm D}}{m_{\rm B} + m_{\rm C} + m_{\rm D}} - x_{\rm A}$$

and the internal coordinates of BCD. To center attention on the CD bond we chose these as the C-D bond distance and the distance from B to the center of mass of CD

$$x_2 = \frac{m_{\rm C} x_{\rm C} + m_{\rm D} x_{\rm D}}{m_{\rm C} + m_{\rm D}} - x_{\rm B}$$
, $x_3 = x_{\rm D} - x_{\rm C}$

For the internal coordinates of the AB+CD products we take them as the two bond dsistances plus the distance between the respective centers of mass

$$z_{1} = \frac{m_{A}x_{A} + m_{B}x_{B}}{m_{A} + m_{B}} - \frac{m_{C}x_{C} + m_{D}x_{D}}{m_{C} + m_{D}} ,$$

$$z_{2} = x_{B} - x_{A} , \quad z_{3} = x_{D} - x_{C}$$

The transformation between the two sets is

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$$\begin{pmatrix} z_1 \\ z_2 \\ z_3 \end{pmatrix} = \begin{pmatrix} \frac{-m_A}{m_A + m_B} & \frac{-m_B M'}{(m_A + m_B)(m_B + m_C + m_D)} & 0 \\ 1 & -\frac{m_C + m_D}{m_B + m_C + m_D} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} , \quad M' = m_A + m_B + m_C + m_D$$

To complete the discussion we note that when no forces act the very same transformation also relates the initial and final velocities

$$\frac{d}{dt} \begin{pmatrix} z_1 \\ z_2 \\ z_3 \end{pmatrix} = \begin{pmatrix} \frac{-m_A}{m_A + m_B} & \frac{-m_B M'}{(m_A + m_B)(m_B + m_C + m_D)} & 0 \\ 1 & -\frac{m_C + m_D}{m_B + m_C + m_D} & 0 \\ 0 & 0 & 1 \end{pmatrix} \frac{d}{dt} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$$

It follows that the only way to change the kinetic energy of the CD bond after the reaction is to put energy in this bond before the reaction. Neither energy from the x_1 motion (the approach of A to BCD) nor from the x_2 motion can affect the vfelocity along z_3 . For the A+BCD \rightarrow AB+CD reaction the unaffected bond is trully a spectator.

Similar considerations apply to the AB+CD \rightarrow AC+BD reaction. In particular one can conclude that relative translation of the reactants cannot contribute energy to the separation of the prodcuts. To drive the reaction one needs initial vibrational excitation of AB and CD.

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