PART E

The questions in Part E test Objectives 1, 17, 18 and 22–24 of Block 2.

Q2.18 Figure 2.1 represents a contour map of the potential energy surface for the hypothetical elementary gas-phase reaction between an atom X· and a diatomic molecule YZ:

$$X\cdot + YZ \longrightarrow XY + Z\cdot \qquad (2.7)$$

assuming a linear arrangement of all three atoms throughout the reaction. With reference to this Figure, select *three* **correct** statements from the key.

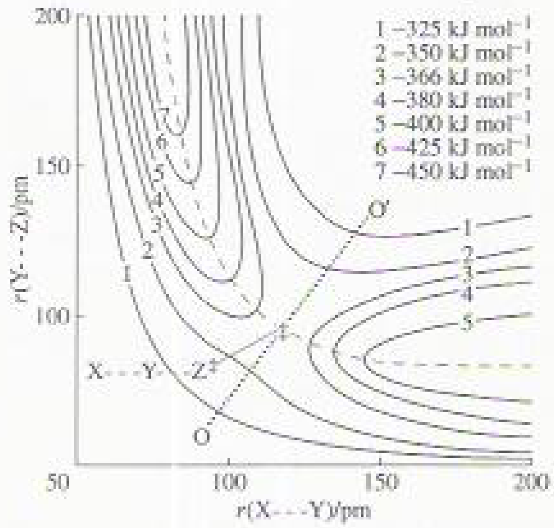

Figure 2.1 A contour map of the potential energy surface for the reaction:

$$X\cdot + YZ \longrightarrow XY + Z\cdot$$

Contours are drawn at energies as labelled on the Figure. The broken line represents the minimum energy path that the reaction can take over the surface. The dotted line OO′ is at right-angles to this pathway at the point corresponding to the activated complex X ---- Y ---- Z‡.

KEY for Q2.18

A During the course of reaction 2.7, the system must follow the lowest-energy path available.

B The rate equation for reaction 2.7 is given by the following expression:

$$J = k_R[X\cdot][YZ]$$

C Reaction 2.7 is exothermic.

D Movement along the line OO′ corresponds to an antisymmetric stretch of the activated complex X ---- Y ----Z‡.

E The activation energy for reaction 2.7 is given by the bond dissociation energy, D, of the YZ molecule.

F The activation energy for reaction 2.7 is greater than that for the *reverse* reaction:

$$Z\cdot + XY \longrightarrow X\cdot + YZ$$

G The Y−Z bond is longer in the activated complex, X ---- Y ---- Z‡, than it is in the YZ molecule.

Q2.19 and Q2.20 These questions are concerned with the elementary gas-phase reaction between bromine atoms, Br·, and ozone, O_3:

$$Br\cdot + O_3 \longrightarrow BrO\cdot + O_2 \qquad (2.8)$$

The reaction is important in the stratosphere as a loss process for ozone. In the stratospheric temperature range (210–260 K) the Arrhenius equation is found to be:

$$k_R = (1.02 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1})\exp(-6.7\,\text{kJ mol}^{-1}/RT)$$

The hard-sphere collision cross-section can be assumed to be 0.65 nm^2, and the molecular masses of Br· and O_3 are:

$$m(Br\cdot) = 13.27 \times 10^{-26}\,\text{kg}$$
$$m(O_3) = 7.97 \times 10^{-26}\,\text{kg}$$

Q2.19 What is the theoretical value of the *A*-factor for reaction 2.8 at 220 K according to the hard-sphere collision theory of chemical reactions? Select from the key the value that is closest to your answer.

KEY for Q2.19

A 1.5×10^8 dm^3 mol^{-1} s^{-1}

B 1.8×10^8 dm^3 mol^{-1} s^{-1}

C 5.8×10^{10} dm^3 mol^{-1} s^{-1}

D 1.1×10^{11} dm^3 mol^{-1} s^{-1}

E 1.5×10^{11} dm^3 mol^{-1} s^{-1}

F 1.8×10^{11} dm^3 mol^{-1} s^{-1}

Q2.20 Use the information provided, together with any data you need from the S342 *Data Book*, to estimate the activation energy for the *reverse* of reaction 2.8. Select from the key the value that is closest to your answer.

KEY for Q2.20

A	41.9 kJ mol^{-1}	E	100.9 kJ mol^{-1}
B	55.3 kJ mol^{-1}	F	122.9 kJ mol^{-1}
C	87.5 kJ mol^{-1}	G	129.6 kJ mol^{-1}
D	94.2 kJ mol^{-1}	H	136.3 kJ mol^{-1}