14.65 a) An elementary reaction is a reaction which cannot be simplified into a series of steps. Instead, it is a single event

b) A unimolecular reaction involves the decomposition or reordering of a single reactant. A bimolecular reaction involves the collision of two reactants.

c) A reaction mechanism is the series of elementary steps that describe how a reaction proceeds from reactants to products.

d) The rate-determining step is the slowest elementary step in a mechanism

14.66

a) An intermediate cannot appear as a reactant in the first step of a mechanism because an intermediate is first created then consumed.

b) Intermediate are represented as a valley on an energy diagram. This makes sense because an intermediate is a product of one step that becomes the reactant for a following step.

c) Cl_2 falling apart is a unimolecular step

14.67

a) unimolecular - rate=$k[Cl_2]$

b) bimolecular - rate=$k[OCl^-][H_2O]$

c) bimolecular - rate=$k[NO][Cl_2]$

14.71 a)

$$H_2 + ICl \Rightarrow HI + HCl$$
$$HI + ICl \Rightarrow I_2 + HCl$$

$$H_2 + ICl + \cancel{HI} + ICl \Rightarrow \cancel{HI} + HCl + I_2 + HCl$$

$$H_2 + 2\ ICl \Rightarrow 2\ HCl + I_2$$

b) HI is an intermediate for this reaction

c) If the first step is the rate determining step, then the rate law for the overall reaction should be the rate law for this first step: rate=$k[H_2][ICl]$

14.74 a)

$$HBr + O_2 \Rightarrow HOOBr$$
$$HOOBr + HBr \Rightarrow 2\ HOBr$$
$$2HOBr + 2HBr \Rightarrow 2H_2O + 2Br_2$$

$$HBr + O_2 + \cancel{HOOBr} + HBr + \cancel{2\ HOBr} + 2\ HBr \Rightarrow \cancel{HOOBr} + \cancel{2\ HOBr} + 2\ H_2O + 2\ Br_2$$

$$4\ HBr + O_2 \Rightarrow 2\ H_2O + 2\ Br_2$$

b) The experimentally determined rate law (rate=k[HBr][O_2]) is the same as the rate law for the first elementary step. As such, the first elementary step (HBr + O_2 ⇒ HOOBr) must be the rate determining step.

c) The intermediates are HOOBr and HOBr.

d) Because HOOBr and HOBr are intermediates, they are understood to be consumed during the reaction. As such, you would not expect to detect them in your products. Therefore, their absence from the products does not disprove the mechanism.