9. Energy Diagrams: First Law of Thermodynamics

The first law of thermodynamics states that energy cannot be created or destroyed: the energy in a system is conserved. For any chemical reaction, the overall change in energy of a system (ΔU) is caused by both the work done to or by the system (w) and the change in temperature (or heat) of the chemicals in the reaction (q). This definition is written as:

$$\Delta U \equiv q + w \tag{1}$$

When a reaction is performed at constant volume, no work can be done and so equation (1) is rewritten as:

$$\Delta U = q_{\rm v} \qquad ({\rm w} = 0) \ (2)$$

where q_v is the heat at constant volume.

Most reactions in chemistry, however, are not done at constant volume, rather they are performed at constant pressure. In this case, work can either be positive (compression - done on the system), negative (expansion – done by the system), or zero (no work). Work is therefore not equal to zero and equation (1) is then rewritten as:

$$\Delta U = q_p + w \qquad (w \neq 0) (3)$$

On energy diagrams, reactions are written as arrows drawn from the energy of the reactants (R) to the energy of the products (P) as seen to the right.

1) On the diagram to the right:

- a) Label the vector that corresponds to the heat at constant volume, q_v . (*Hint: Remember*, $\Delta U = q_v$)
- b) Draw and label the vector that corresponds to the heat at constant pressure (*Hint: Remember*, $\Delta U = q_p + w$).
- c) When is the heat greater in magnitude, at constant volume or constant pressure? Explain.

2) On the diagram to the right, draw the vectors that corresponds to the heat at constant pressure (q_p) , the change in internal energy (ΔU) , and the heat at constant volume (q_v) .



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3) Draw an energy diagram for a compression reaction that is exothermic, such that the constnat volume heat is 90 kJ and 10 kJ of work are put into the system. What is the heat at constant pressure?



5) In the diagram you drew to the right, explain what makes this reaction a compression.