Thermochemistry and Its Applications

- Some consequences of the first law will now be explored.
 - Thermochemistry deals with how changes in temperature and energy are related.
 - Conditions under which the process occurs must be defined carefully.
 - Heat released by a chemical processes will vary according to the constraints of the process.
 - This is because heat is a path function.
 - Specific types of energy changes will be defined.
 - Standard states will be defined.
 - Also considered will be the molecular interpretation of thermochemical data.

Heat Capacity and Enthalpy

- Consider a vessel with rigid and adiabatic walls, filled with fluid.
 - The system is isolated except for a heater.
 - At equilibrium the temperature of the fluid is T_1 .
 - Current is passed through the heater for a specified time and the electrical energy is dissipated as quantity of heat q.
 - A new equilibrium is established at T_2 .
 - Vessel is rigid, therefore constant V process.
 - The heat capacity at constant V may be defined as:

$$C_V = \lim_{\Delta T \to 0} \left(\frac{q}{\Delta T}\right)_V$$

By the first law of thermodynamics:

$$\Delta U = q_V$$

since pV work is zero at constant V.

Therefore

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

- Now consider the same process, but now allow one wall of the container to be a freely moving, but adiabatic, piston.
 - The volume of the system can change as heat is added.

- Continued:
 - The process will occur at constant p if external pressure is fixed at p_{app} and heat is added so slowly (i.e. reversibly) that at all points $p = p_{app}$.
 - The heat capacity at constant p may be defined as:

$$C_p = \lim_{\Delta T \to 0} \left(\frac{q}{\Delta T}\right)_p$$

- Heat capacity may also be defined with respect to other constraints, but C_p and C_V are the most widely used.
 - Heat capacities are extensive (J K^{-1}).
 - Often defined with respect to particular amounts of a substance:

- Continued:
 - Molar heat capacity is the heat capacity per mole (J K⁻¹ mol⁻¹).
 - Specific heat is (usually) heat capacity per gram (J $K^{-1} g^{-1}$).
- Molar heat capacity (once the path has been specified) can be treated as a state function characteristic of the particular substance.
 - It depends on the energy spectrum of the substance.
- The convention of the text is to use uppercase letters for extensive quantities and lower case for the molar quantities.
 - *U* is internal energy.

- Continued:
 - u is the molar internal energy. (Other texts use \overline{U} for molar internal energy.)
- Consider a constant pressure experiment in which the fluid is allowed to expand.
 - Work, w_p , is negative since work is done on the surroundings.
 - Therefore adding a given quantity of energy to the system causes a smaller internal energy change than in the case when the volume is held constant and no work is done on the surroundings.
 - In the constant volume case, all the heat added to the system is used to increase the internal energy of the system.

- Thus for the same value of q, $(\Delta U)_p < (\Delta U)_V$, $(\Delta T)_p < (\Delta T)_V$, and $C_p > C_V$.
- For a constant volume process $(dU)_V = C_V dT$.
- From the first law in differential form:

$$(dU)_p = C_p \ dT - p \ dV$$

which describes a reversible constant pressure process of a system that can do only pV work.

- This can be rewritten as $C_p dT = (dU + pdV)_p$.
- This in turn suggests a new thermodynamic variable, *H*, or enthalpy:

$$H \equiv U + pV$$

• The differential of H at constant p:

$$(dH)_p = (dU + pdV)_p = C_p dT$$

and thus

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

and the heat transferred in a constant pressure process is:

$$q_p = (\Delta H)_p$$

- Because U and pV are also state functions, H is a state function.
- Enthalpy is convenient as a state function to describe processes carried out at constant pressure.

- Enthalpy along paths other than constant p many be considered.
 - For example for constant V,

 $(dH)_V = (dU)_V + d(pV)_V = C_V dT + V dp$

- Enthalpy is usually determined with a calorimeter.
 - Calorimetry can also be used to determine heat capacity.
 - C_p and C_V are usually determined as functions of temperature and pressure over the ranges of interest.
 - C_p and C_V are related to each other.



Figure 14.1 Temperature dependence of the heat capacity for various substances. (a) Room-temperature gases and liquids. (b) Room-temperature solids.

For a perfect gas:

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$
$$= \left[\frac{\partial (U + pV)}{\partial T}\right]_P - \left(\frac{\partial U}{\partial T}\right)_V$$
$$= \left[\frac{\partial (pV)}{\partial T}\right]_P = \left[\frac{\partial (nRT)}{\partial T}\right]_P = nR$$

In the gas phase, $C_p - C_V$ can be significant.

- In condensed phases, pV is much smaller than nRT, so C_p and C_V are similar.
- $C_p C_V$ will be explored further in Chapter 17.



392 • Thermochemistry and Its Applications

Heat capacities are usually dependent on temperature and are expressed in the form:

$$c_P = a + bT + cT^2$$

for the phase of interest.

Energy and Enthalpy Changes in Chemical Reactions

- Consider a general chemical reaction of the form: $aA + bB + \cdots = IL + mM + \cdots$
- This may be rewritten as:

IL + mM + · · · · aA - bB - · · · = $\sum_{i=1}^{r} \nu_i X_i = 0$ where X_i represents the species and ν_i represents the stoichiometric coefficients.

- Continued:
 - By convention $\nu_i < 0$ for reactants and $\nu_i > 0$ for products. Thus for

$$\frac{1}{2}$$
 H₂ + $\frac{1}{2}$ Cl₂ = HCl

•
$$\nu_{\text{HCl}} = 1$$

• $\nu_{\text{H}_2} = -\frac{1}{2}$
• $\nu_{\text{Cl}_2} = -\frac{1}{2}$

In terms of this notation, the condition of conservation of mass becomes:

$$\Delta M = \sum_{i=1}^{r} \nu_i M_i = 0$$

where M_i is the molar mass of substance *i*.

• Consider now internal energy U and enthalpy H

$$\Delta U = \sum_{i=1}^{r} \nu_i u_i$$

$$\Delta H = \sum_{i=1}^{r} \nu_i h_i$$

where u_i and h_i are the internal energy and enthalpy per mole of component *i*.

- Note now that ΔU and ΔH are with respect to the stoichiometry of the reaction.
- The text then goes on to connect this to Hess's Law.

Thermochemistry of Physical Processes

- Consider the changes in U and H for a fluid initially in equilibrium at p_1, V_1, T_1 moving to a new equilibrium at p_2, V_2, T_2 .
 - U and H are state functions, therefore the values of ΔU and ΔH are independent of the path between the initial and final state.
- Consider a path from the initial state and the final state that consists of two steps:
 - An isochor: the fluid is heated or cooled at constant V to T_2 .
 - An isotherm: the fluid is held at constant temperature T_2 and the volume is changed until V_2 is reached.
- ΔU may be calculated on this path.



Figure 14.3 Two-step analysis of the change of state of a fluid: (a) constant-volume process followed by constant-temperature process, for calculating ΔU ; (b) constant-pressure process followed by constant-temperature process, for calculating ΔH . In both cases the change is from the initial state p_1 , V_1 , T_1 to the final state p_2 , V_2 , T_2 .

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• An infinitesimal change in U is given by:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

where dT and dV are the infinitesimal changes in T and V.

• ΔU can be determined by integrating over this path:

$$\Delta U = U(T_2, V_2) - U(T_1, V_1)$$
$$= \int_{T_1, V_1}^{T_2, V_1} \left(\frac{\partial U}{\partial T}\right)_V dT + \int_{T_2, V_1}^{T_2, V_2} \left(\frac{\partial U}{\partial V}\right)_T dV$$

The first step takes place at constant V. Therefore:

$$\Delta U_{\text{first step}} = \int_{T_1, V_1}^{T_2, V_1} \left(\frac{\partial U}{\partial T}\right)_V dT = \int_{T_1, V_1}^{T_2, V_1} C_V dT$$

The second step takes place at constant T. Therefore:

$$\Delta U_{\text{second step}} = \int_{T_2, V_1}^{T_2, V_2} \left(\frac{\partial U}{\partial V}\right)_T dV$$

• To evaluate this, $(\partial U/\partial V)_T$ needs to be determined.

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Thus for the total internal energy change:

$$\Delta U = \int_{T_1,V_1}^{T_2,V_1} \left(\frac{\partial U}{\partial T}\right)_V dT = \int_{T_1,V_1}^{T_2,V_1} C_V dT + \int_{T_2,V_1}^{T_2,V_2} \left\{ T\left(\frac{\partial p(T,V)}{\partial T}\right)_V - p(V,T) \right\} dV$$

- This can be evaluated if the heat capacity C_V and the equation of state are known.
- If the equation of state is not known, then measurements of p and T at constant V may be used to evaluate $(\partial U/\partial V)_T$.

- To determine the enthalpy change, a different two step path is more convenient:
 - An isobar: the fluid is heated or cooled at constant p to T₂.
 - An isotherm: the fluid is held at constant temperature and the pressure is changed until p_2 is reached.
- An infinitesimal change in H is given by:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

It can be shown that:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p$$

• Thus the total enthalpy change, ΔH , may be determined:

$$\Delta H = H(T_2, p_2) - H(T_1, p_1)$$

$$= \int_{T_1, p_1}^{T_2, p_1} \left(\frac{\partial H}{\partial T}\right)_p dT + \int_{T_2, p_1}^{T_2, p_2} \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$= \int_{T_1, p_1}^{T_2, p_1} C_p dT$$

$$+ \int_{T_2,p_1}^{T_2,p_2} \left\{ V(p,T) - T\left(\frac{\partial V(T,p)}{\partial T}\right)_p \right\} dp$$

 \checkmark When work other than pV work is involved:

$$dU = d\bar{q} + d\bar{w}_{pV} + d\bar{w}_X$$

$$dH = (d\bar{q})_p + d\bar{w}_X$$

 \blacksquare Hess's Law applies to the heat capacities, C_p and C_V .

Introduction to Phase Changes

This section will be omitted (for now).

Standard States

This section is to be reviewed, but not in class.

Thermochemistry of Solutions

This section is to be reviewed, but not in class.

Molecular Interpretation of Physical Processes

- This section is to be reviewed, but not in class.
 Bond Energies
- This section is to be reviewed, but not in class.

Some Energy Effects in Molecular Structures

This section is to be reviewed, but not in class.

Lattice Energies of Ionic Crystals

This section is to be reviewed, but not in class.

involves a phase change corresponds to a path crossing one



Figure 14.4 A typical phase diagram for a simple substance. The lines represent the locus of pressure and temperature for which two phases can coexist, for example liquid and vapor along the line *TP-C*. The points *TP* and *C* are, respectively, the triple point and the critical point for the substance (see Chapter 24).

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Figure 14.6 Heat of solution of HCl in water.



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