The Thermochemistry of Physical Change

– phase changes:

solid ↔ liquid liquid ↔ gas solid ↔ gas

6.9 Vaporization

– vaporization (liquid → gas)

– condensation (gas → liquid)

- Vaporization is endothermic - the system absorbs energy needed to overcome the attractive forces between the molecules in the liquid in order to spread them apart in the vapor

- **Enthalpy of vaporization** (DH_{vap}) - the enthalpy change accompanying the conversion of one mole of a liquid into vapor

$$DH_{vap} = H_{vapor} - H_{liquid}$$

$DH_{vap} > 0$ (endothermic)

- **Enthalpy of condensation** (DH_{cond})

$$DH_{cond} = H_{liquid} - H_{vapor} = -DH_{vap}$$

$DH_{cond} < 0$ (exothermic)

- The DH for the reverse of any process is the negative of the DH for the forward process (because H is a state function)

Example: The vaporization of **23 g** of ethanol at 78.5°C and 1 atm requires **22 kJ** of energy supplied as heat. Calculate the enthalpy of vaporization of ethanol.

P = constant ⇒ $DH = q$ = 22 kJ

need DH per 1 mol of ethanol

$$n = 23 \text{ g ethanol} \times \left(\frac{1 \text{ mol ethanol}}{46.1 \text{ g ethanol}} \right) = 0.50 \text{ mol ethanol}$$

$$\Delta H_{vap} = \frac{22 \text{ kJ}}{0.50 \text{ mol}} = 44 \text{ kJ/mol}$$

6.10 Melting and Sublimation

– melting, fusion (solid → liquid)

– freezing (liquid → solid)

- **Enthalpy of fusion** (DH_{fus}) - the enthalpy change accompanying the conversion of one mole of a solid into liquid

$$DH_{fus} = H_{liquid} - H_{solid} = -DH_{freez}$$

- Melting is endothermic - energy is needed to overcome the forces holding the particles of a solid in position and form the mobile liquid

⇒$DH_{fus} > 0$ (endothermic); $DH_{freez} < 0$ (exothermic)

– sublimation (solid → gas)

– deposition (gas → solid)

- **Enthalpy of sublimation** (DH_{sub}) - the enthalpy change accompanying the conversion of one mole of a solid into vapor

$$DH_{sub} = H_{vapor} - H_{solid} = -DH_{depos}$$

- Sublimation is endothermic - energy is needed to overcome the forces holding the particles of a solid in position and form the gas phase

⇒$DH_{sub} > 0$ (endothermic); $DH_{depos} < 0$ (exothermic)

For H_2O DH_{fus} = 6.0 kJ/mol and DH_{sub} = 50 kJ/mol

$DH_{vap} = H_{vapor} - H_{liquid}$

$DH_{fus} = H_{liquid} - H_{solid}$

$DH_{sub} = H_{vapor} - H_{solid}$

$DH_{vap} + DH_{fus} = H_{vapor} - H_{liquid} + H_{liquid} - H_{solid} =$
$= H_{vapor} - H_{solid} = DH_{sub}$

⇒ $DH_{vap} + DH_{fus} = DH_{sub}$
(true only at constant T)

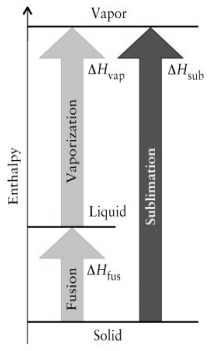

Fig. 6.26

6.11 Heating and Cooling Curves

- **Heating (or cooling) curve** - a graph of the temperature of a sample as a function of the heat added to (or removed from) it.
- Regions in the heating (cooling) curves
  - sloped regions - correspond to temperature changes in the pure solid, liquid or gas phases (slope depends on the heat capacity of each phase)
  - flat regions - correspond to phase changes (temperature remains constant)

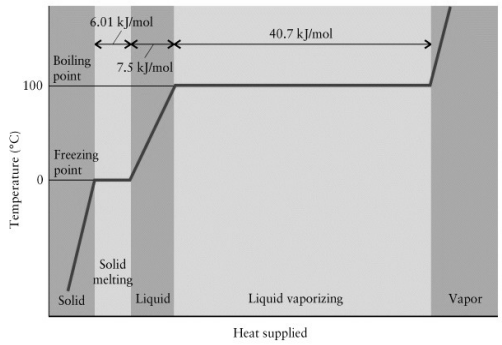

Fig. 6.27

The Enthalpy of Chemical Change

6.12 Reaction Enthalpies

- Thermochemical equations - chemical equation with physical states + enthalpy change (***DH***)

  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

  ***DH* = – 890 kJ**

  the *DH* is for 1 mol CH_4 and 2 mol of O_2
- The value of ***DH*** depends on the way the chemical equation is written (stoichiometric coefficients)

- Reaction enthalpy (***DH*$_r$**) - ***DH*** reported per one mol of a given reactant or product
- Properties of thermochemical equations
  - multiplying an equation by a number multiplies the ***DH*** value by the same number
  - reversing the direction of a reaction changes the sign of the ***DH*** value

$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

***DH* = – 2×890 kJ**

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$

***DH* = + 890 kJ**

- **Example:** When **2.31 g** of solid **P** reacts with gaseous **Cl_2** to form liquid **PCl_3** in a constant pressure calorimeter with ***C* = 2.16 kJ/°C**, the temperature rises by **11.06°C**. Write the thermochemical equation.

  q_{surr} = *C*×*DT* = 2.16 kJ/°C× 11.06°C = 23.9 kJ

  ***P* = constant**

⇒ *DH* = q_{sys} = – 23.9 kJ (for 2.31 g P)

Chem. Eq. $2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(g)$

⇒ need *DH* for 2 mol P

$$2.31\ \text{g P} \times \left(\frac{1\ \text{mol P}}{30.97\ \text{g P}} \right) = 7.46 \times 10^{-2}\ \text{mol P}$$

$$\Delta H_r = \frac{-23.9\ \text{kJ}}{7.46 \times 10^{-2}\ \text{mol P}} = -320.\ \text{kJ/mol P}$$

$$\Delta H = \frac{-320\ \text{kJ}}{1\ \text{mol P}} \times 2\ \text{mol P} = -641\ \text{kJ}$$

$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(g)$ *DH* = – 641 kJ

6.13 Standard Reaction Enthalpies

- DH_r depends on the physical states of reactants an products, ***P*** and ***T***
- **Standard state** - the state of a substance in its pure form at **1 atm** and a given temperature (usually **298 K**). For substances in solutions, the standard state is at concentrations **1 mol/L**
- **Standard reaction enthalpy** (DH_r^o) - DH_r for a reaction in which all reactants and products are in their standard states

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

$DH = -802$ kJ

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$DH^o = -890$ kJ

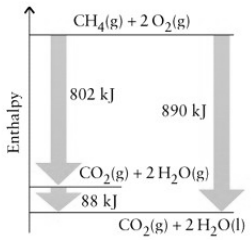

Fig. 6.29