

Lecture 23

I. DH for Chemical Rxns

II. DH for Phase changes

III. DH for Temperature changes

IV. Combinations – Chemical, Phase, and Temperature Changes

I. ΔH for Chemical Rxns

Enthalpies of Formation = $\Delta_f H^0$ = standard enthalpy for formation of substance from elements in their reference (naturally occurring) states at 1 bar (1.01 bar = 1 atm). Note keep in mind these should be computed stoichiometrically, i.e. *you must convert from “per moles of substance” to “per moles of reaction.”*

i.e. $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ $\Delta H^0 = -285.83 \text{ kJ (mol rxn)}^{-1}$

$\Delta H^0 = \Delta_f H^0_{H_2O(l)} \times n_{H_2O(l)} / 1 \text{ mol rxn} - [\Delta_f H^0_{H_2(g)} \times n_{H_2(g)} / 1 \text{ mol rxn} +$

$\Delta_f H^0_{O_2(g)} \times n_{O_2(g)} / 1 \text{ mol rxn}]$

$= -285.83 \text{ kJ (mol H}_2\text{O)}^{-1} \times 1 \text{ mol H}_2\text{O} / 1 \text{ mol rxn} - [0 \text{ kJ (mol H}_2\text{)}^{-1} \times 1 \text{ mol H}_2 / 1 \text{ mol rxn} + 0 \text{ kJ (mol O}_2\text{)}^{-1} \times ? \text{ mol O}_2 / 1 \text{ mol rxn}] = -285.83 \text{ kJ (mol rxn)}^{-1}$

Note the enthalpy of formation of elements in their naturally occurring states is zero.

Note that the answer was computed “intensively”, so that if we had a quantity of any substance in the reaction, we could determine extensive enthalpy changes easily.

Example: Show that for $H_2O(l) + N_2O_5(g) \rightarrow 2HNO_3(g)$ the $\Delta H^0_{rxn} = -73.7 \text{ kJ (mol rxn)}^{-1}$

given: $\Delta_f H^0_{HNO_3(g)} = -174.10 \text{ kJ (mol HNO}_3\text{)}^{-1}$

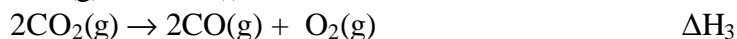
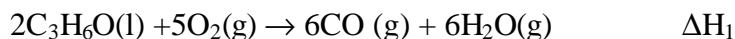
$\Delta_f H^0_{H_2O(l)} = -285.83 \text{ kJ (mol H}_2\text{O)}^{-1}$

$\Delta_f H^0_{N_2O_5(g)} = 11.3 \text{ kJ (mol N}_2\text{O}_5\text{)}^{-1}$

This is horizontal approach.

What's another way to find ΔH^0_{rxn} without having to carryout exp'ts: Same as when we dealt with internal E

Example: Show that ΔH of may be expressed as $\Delta H_1/2 + 3\Delta H_2 + -3/2\Delta H_3$ for the following reaction: $C_3H_6O(l) + 4 O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$

II. ΔH for Phase changes

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H^0 = \Delta H_{vap} = \Delta_f H^0(H_2O(g)) - \Delta_f H^0(H_2O(l)) = -241.82 - (-285.83)$
 $= 44.01 \text{ KJ mol}^{-1}$

Example: Compute the ΔH for 4.50 grams of $H_2O(g)$ condensing to $H_2O(l)$?

III. ΔH for Temperature changes

$$\Delta H = q_p = (\text{mass or moles}) C_p(\text{per mass or per mole}) \Delta T$$

Simply use the above expression and dimensional analysis!

Example: What is the change in enthalpy as 55.2 grams of $H_2O(l)$ is cooled from $99.5^\circ C$ to $1.23^\circ C$ at constant pressure given $C_{p,m} = 75.291 J K^{-1} mol^{-1}$?

$$\text{Answer: } 55.2 \text{ g} \left(\frac{1 \text{ mole}}{18 \text{ g}} \right) (75.291 \text{ J K}^{-1} \text{ mol}^{-1}) (1.23^\circ C - 99.5^\circ C) \left(\frac{1 \text{ K}}{1^\circ C} \right) = -22689 \text{ Joules}$$

- Note the last conversion of C to K. A *change* of x degrees C is equal to a *change* of x degrees Kelvin, only the offset differs.
- Note the negative sign, indicative that the enthalpy of the system is lowered.

Example: If the $C_{p,m}$ of methanol gas is $43.89 J K^{-1} mol^{-1}$ determine the heat needed to increase the temperature of 3.56 g of methanol from $45.4^\circ C$ to $56.7^\circ C$ at constant pressure?

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IV. Combinations – Chemical, Phase, and Temperature Changes**Example: Combing phase change and temperature change**

Show that the 7080 J of heat at constant pressure is needed to heat 2.54 grams of liquid water at $25.0^\circ C$ to water vapor at $115.0^\circ C$. $C_{p,m} = 75.291 J K^{-1} mol^{-1}$ for liquid water, and $C_{p,m} = 33.58 J K^{-1} mol^{-1}$ for gaseous water?

Answer: Divide this problem into 3 parts:

- (1) ΔH for heating liquid water from $25.0^\circ C$ to $100^\circ C$.
- (2) ΔH for liquid to gas phase transition: $\Delta_{\text{vap}}H$ at $100^\circ C$.
- (3) ΔH for heating gaseous water from $100.0^\circ C$ to $115.0^\circ C$.

Example: Sketch 5 the steps necessary to determine the heat necessary to heat 10 grams of ice at $-10^\circ C$ to $110^\circ C H_2O(g)$.

Example: Combing chemical reaction and temperature changes

Used to find ΔH_T° of a reaction at T given $\Delta H_{T_0}^\circ$

$$D H^{\circ} = H^{\circ}_{PROD} - H^{\circ}_{REACT} \text{ (stoichiometrically)}$$

$$D C_p = C_{PROD} - C_{REACT} \text{ (stoichiometrically)}$$

$$\text{by def } D H^{\circ} = C_p DT$$

$$D H^{\circ}_T = D H^{\circ}_{T_0} + C_{p,prod1}^{\circ} n_{prod1} (T - T_0) + C_{p,prod2}^{\circ} n_{prod2} (T - T_0) + \dots \\ - C_{p,react1}^{\circ} n_{react1} (T - T_0) - C_{p,react2}^{\circ} n_{react2} (T - T_0) + \dots$$

$$\searrow D H^{\circ}_T = D H^{\circ}_{T_0} + D C_p^{\circ} (T - T_0) = D H^{\circ}_{T_0} + D C_p^{\circ} DT$$

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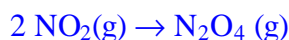
Another way to arrive at this is to employ Hess's Law.

For example, if you desired to compute the total enthalpy $\Delta H^{\circ}(T_2)$ needed for a chemical reaction $A(T_2) \rightarrow B(T_2)$ at a new temperature T_2 , given $A(T_1) \rightarrow B(T_1)$, $\Delta T = T_2 - T_1$.

$$\begin{array}{ll} A(T_1) \rightarrow B(T_1) & \Delta H^{\circ}(T_1) \\ B(T_1) \rightarrow B(T_2) & C_p^{(B)} \Delta T \\ \underline{A(T_2) \rightarrow A(T_1)} & - C_p^{(A)} \Delta T \\ A(T_2) \rightarrow B(T_2) & \Delta H^{\circ}(T_2) = \Delta H^{\circ}(T_1) + (C_p^{(B)} - C_p^{(A)}) \Delta T \end{array}$$

Thus compute the ΔH at the standard temperature given in the table (273.15 or 298.15 K) and add the physical change up heating (cooling) reactants/products to the new temperature. Note keep in mind these should be computed stoichiometrically, i.e. *you must convert from "per moles of substance" to "per moles of reaction."*

For example show that the ΔH at 100°C is $-56.98 \text{ kJ mol}^{-1}$ for the reaction:



given $\Delta_f H^{\circ}$ of $\text{NO}_2(\text{g})$ at 298.15 = $33.18 \text{ kJ mol}^{-1}$, $\Delta_f H^{\circ}$ of $\text{N}_2\text{O}_4(\text{g})$ at 298.15 K = 9.16 kJ mol^{-1} , $C_{p,m}$ of $\text{NO}_2(\text{g})$ = $37.20 \text{ J K}^{-1} \text{ mol}^{-1}$, $C_{p,m}$ of $\text{N}_2\text{O}_4(\text{g})$ = $77.28 \text{ J K}^{-1} \text{ mol}^{-1}$

Answer:

$$\Delta H^{\circ}_{100\text{C}} = \Delta H^{\circ}_{0\text{C}} + \Delta C_{p,m} \Delta T$$

$$\Delta H^{\circ}_{0\text{C}} = 9.16 \text{ kJ (mol N}_2\text{O}_4)^{-1} \times 1 \text{ mol N}_2\text{O}_4/\text{mol rxn} - 33.18 \text{ kJ (mol NO}_2)^{-1} \times 2 \text{ mol NO}_2/\text{mol rxn} = -57.20 \text{ kJ (mol rxn)}^{-1}$$

$$\Delta C_{p,m} = 77.28 \text{ J K}^{-1} \text{ mol}^{-1} (\text{mol N}_2\text{O}_4)^{-1} \times 1 \text{ mol N}_2\text{O}_4/\text{mol rxn} - 37.20 \text{ J K}^{-1} \text{ mol}^{-1} (\text{mol NO}_2)^{-1} \times 2 \text{ mol NO}_2/\text{mol rxn} = 2.88 \text{ J K}^{-1} (\text{mol rxn)}^{-1}$$

$$\Delta T = 100^{\circ}\text{C} - 25^{\circ}\text{C} \times (1 \text{ } \Delta\text{K}/1\Delta^{\circ}\text{C}) = 75 \text{ K}$$

$$\Delta C_{p,m} \Delta T = 2.88 \text{ J K}^{-1} (\text{mol rxn)}^{-1} \times 75 \text{ K} = 216 \text{ J mol}^{-1} = 0.216 \text{ kJ (mol rxn)}^{-1} \quad \Delta H^{\circ}_{100\text{C}} = \Delta H^{\circ}_{0\text{C}} + \Delta C_{p,m} \Delta T = -57.20 \text{ kJ (mol rxn)}^{-1} + 0.216 \text{ kJ (mol rxn)}^{-1} = -56.98 \text{ kJ (mol rxn)}^{-1}$$

COMBINATIONS INVOLVING ALL 3 – very involved: sketch the steps first