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**

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

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

$\Delta H^0 = \Delta_f H^0_{H2O(l)} \times n_{H2O(l)} / 1$ mol rxn $- [\Delta_f H^0_{H2(g)} \times n_{H2\,(g)} / 1$ mol rxn + $\Delta_f H^0_{O2(g)} \times n_{O2\,(g)} / 1$ mol rxn]

= **-285.83** kJ (mol $H_2O)^{-1}\times 1$ mol H_2O / 1 mol rxn - [**0** kJ (mol $H_2)^{-1}\times 1$ mol H_2 / 1 mol rxn + **0** kJ (mol $O_2)^{-1}\times$? mol O_2 / 1 mol rxn] = **-285.83** 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 **$H_2O(l) + N_2O_5(g)$ ® $2HNO_3(g)$** the ΔH^0_{rxn} = -73.7 kJ (mol rxn)$^{-1}$

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

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

$\Delta_f H^0$ $N_2O_5(g)$ = 11.3 kJ (mol $N_2O_5(g))^{-1}$

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: $C_3H_6O(l) + 4\,O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$

$2C_3H_6O(l) + 5O_2(g) \rightarrow 6CO\,(g) + 6H_2O(g)$	ΔH_1
$H_2O(g) \rightarrow H_2O(l)$	ΔH_2
$2CO_2(g) \rightarrow 2CO(g) + O_2(g)$	ΔH_3

II. ΔH for **Phase changes**

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

$\Delta H = q_p$ = (mass or moles) Cp(per mass or per mole) ΔT
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 ^{0}C to 1.23^{0}C at constant pressure given $C_{p,m}$ = 75.291 J K^{-1} mol^{-1}?

Answer: $55.2\boldsymbol{g}\left(\frac{1\boldsymbol{mole}}{18\boldsymbol{g}}\right)(75.291\boldsymbol{J}\,\boldsymbol{K}^{-1}\boldsymbol{mol}^{-1})(1.23^0\boldsymbol{C} - 99.5^0\boldsymbol{C})\left(\frac{\Delta 1\boldsymbol{K}}{\Delta 1^0\boldsymbol{C}}\right) = -22689\ \boldsymbol{Joules}$

- 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 ^{0}C to 56.7 ^{0}C at constant pressure?

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 ^{0}C to water vapor at 115.0 ^{0}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 ^{0}C to 100 ^{0}C.
(2) ΔH for liquid to gas phase transition: $\Delta_{vap}H$ at 100 ^{0}C.
(3) ΔH for heating gaseous water from 100.0 ^{0}C to 115.0 ^{0}C.

Example: Sketch 5 the steps necessary to determine the heat necessary to heat10 grams of ice at –10^{0}C to 110^{0}C $H_2O(g)$.

Example: Combing chemical reaction and temperature changes

Used to find $\Delta \boldsymbol{H}^0_{\boldsymbol{T}}$ of a reaction at T given $\Delta \boldsymbol{H}^0_{\boldsymbol{T_0}}$

$$\Delta H^0 = H^0_{PROD} - H^0_{REACT}\ (stoichiometrically)$$
$$\Delta C_p = C_{PROD} - C_{REACT}\ (stoichiometrically)$$

$$by\ def\ \Delta H^0 = C_p \Delta T$$
$$\Delta H^0_T = \Delta H^0_{T_0} + C^0_{p,prod1} n_{prod1}(T - T_0) + C^0_{p,prod2} n_{prod2}(T - T_0) + \ldots$$
$$- C^0_{p,react1} n_{react1}(T - T_0) - C^0_{p,react2} n_{react2}(T - T_0) + \ldots$$

$$\therefore \quad \Delta H^0_T = = \Delta H^0_{T_0} + \Delta C^0_p (T - T_0) = \Delta H^0_{T_0} + \Delta C^0_p \Delta T$$

Another way to arrive at this is to employ Hess's Law.
For example, if you desired to compute the total enthalpy $\Delta H^0(T_2)$ needed for a chemical reaction $A(T_2) \rightarrow B(T_2)$ at a new temperature T_2, given $A(T_1) \rightarrow B(T_1)$, $\Delta T = T_2 - T_1$.

$A(T_1) \rightarrow B(T_1)$	$\Delta H^0(T_1)$
$B(T_1) \rightarrow B(T_2)$	$C_p^{(B)}\ \Delta T$
$\underline{A(T_2) \rightarrow A(T_1)}$	$- C_p^{(A)}\ \Delta T$
$A(T_2) \rightarrow B(T_2)$	$\Delta H^0(T_2) = \Delta H^0(T_1) + (C_p^{(B)} - C_p^{(A)})\ \Delta T$

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 stoichometrically, i.e. *you must convert from "per moles of substance" to "per moles of reaction."*
For example show that the ΔH at 100^0C is –56.98 kJ mol^{-1} for the reaction:

$$2\ NO_2(g) \rightarrow N_2O_4\ (g)$$

given $\Delta_f H^0$ of $NO_2(g)$ at 298.15 = 33.18 kJ mol^{-1} , $\Delta_f H^0$ of $N_2O_4(g)$ at 298.15 K = 9.16 kJ mol^{-1}, $C_{p,m}$ of $NO_2(g)$ = 37.20 J K^{-1} mol^{-1}, $C_{p,m}$ of $N_2O_4(g)$ = 77.28 J K^{-1} mol^{-1}
Answer:
$\Delta H^0_{100C} = \Delta H^0_{0C} + \Delta C_{p,m}\Delta T$

ΔH^0_{0C} = 9.16 kJ $(mol\ N_2O_4)^{-1}$×1 mol N_2O_4/mol rxn - 33.18 kJ $(mol\ NO_2)^{-1}$×2 mol NO_2/mol rxn = -57.20 kJ $(mol\ rxn)^{-1}$

$\Delta C_{p,m}$= 77.28 J K^{-1} mol^{-1} $(mol\ N_2O_4)^{-1}$×1 mol N_2O_4/mol rxn - 37.20 J K^{-1} mol^{-1} $(mol\ NO_2)^{-1}$×2 mol NO_2/mol rxn = 2.88 J K^{-1} $(mol\ rxn)^{-1}$
$\Delta T = 100^0C - 25^0C \times (1\ \Delta K/1\Delta^0 C) = 75$ K
$\Delta C_{p,m}\Delta T$ = 2.88 J K^{-1} $(mol\ rxn)^{-1}$ × 75 K = 216 J mol^{-1} = 0.216 kJ $(mol\ rxn)^{-1}$ $\Delta H^0_{100C} = \Delta H^0_{0C} + \Delta C_{p,m}\Delta T$ = -57.20 kJ $(mol\ rxn)^{-1}$ + 0.216 kJ $(mol\ rxn)^{-1}$ = -56.98 kJ $(mol\ rxn)^{-1}$
<u>COMBINATIONS INVOLVING ALL 3</u> – very involved: sketch the steps first