Chapter 6 - Thermodynamics: The First Law

Equations Summary

A. First Law (*Review statements summarized on web page*)

Internal Energy, U

ANY SYSTEM $\Delta U = -\Delta U_{surroundings}$

ISOLATED SYSTEM $\Delta U = 0$

CLOSED SYSTEM $\Delta U = q + w$

FOR PRESSURE-VOLUME WORK ONLY $w = -\int P_{ext} dV$

AT CONSTANT PRESSURE $w = -P_{ext}\Delta V$

AT CONSTANT VOLUME $w = 0$

$\Delta U = q + 0 = q$

$\Delta U = q_v$

HEAT ABSORBED OR RELEASED AT CONSTANT VOLUME

Derived energy, ***Enthalpy,*** H

$H \equiv U + PV$

$\Delta H = \Delta U + \Delta(PV)$

AT CONSTANT PRESSURE $\Delta(PV) = P\Delta V$

$\Delta H = \Delta U + P\Delta V$

$= (q - P\Delta V) + P\Delta V = q$

$\Delta H = q_p$

HEAT ABSORBED OR RELEASED AT CONSTANT PRESSURE

B. Heat or Cool Substance $q = C\Delta T = m\,C_s\,\Delta T = n\,C_n\,\Delta T$

C. Calorimetry $-q_{process} = q_{water} + q_{calorimeter}$

MEASURE HEAT FLOW FOR CHEMICAL REACTION OR PHYSICAL CHANGE

TRANSFER TO SOMETHING EASY TO MEASURE → CHANGE IN TEMPERATURE IN WATER.

HEAT LOST BY CHANGE = HEAT GAINED BY WATER AND CALORIMETER

BOMB CALORIMETER	CONSTANT VOLUME	$q = q_v = \Delta U$	$q_{calorimeter}$ large
"COFFEE CUP" CALORIMETER	CONSTANT PRESSURE	$q = q_p = \Delta H$	$q_{calorimeter}$ small

D. Phase Change $q = n\,\Delta H_{phase}$ (*CONSTANT PRESSURE*)

TEMPERATURE CONSTANT ---> Avg KE constant. PE changes.

$\Delta H_{fusion} << \Delta H_{vaporization} < \Delta H_{sublimation}$

Sketch a general heating curve. Label. Show how to calculate q for each step.

E. Calculating Standard Enthalpy of Reaction (*Review def standard state, standard formation reaction*)

BASED ON HESS'S LAW

FROM STANDARD ENTHALPIES OF FORMATION $\Delta H^0_{rxn} = \sum n_i\,\Delta H^0_f(\text{products}) - \sum n_j\,\Delta H^0_f(\text{reactants})$

FROM BOND ENERGIES $\Delta H^0_{rxn} \approx \sum n_i\,BE(\text{reactants}) - \sum n_j\,BE(\text{products})$

E_{in} *(BREAK)* E_{out} *(MAKE)*

If BE reactants > products ? ... If BE reactants < products ?

Sketch a reaction coordinate diagram endo/exothermic. Label