PROBLEM-SOLVING TACTICS

If we have a simple chemical equation with the variables A, B and C representing different compounds: $A+B \rightleftharpoons C$

and we have the standard enthalpy of formation values as such:

$$\Delta H_f^{\circ}[A] = 433 \text{ KJ/mol}$$
$$\Delta H_f^{\circ}[B] = -256 \text{ KJ/mol}$$
$$\Delta H_f^{\circ}[C] = 523 \text{ KJ/mol}$$

The equation for the standard enthalpy change of formation is as follows:

$$\Delta H^{\circ}_{reaction} = \Delta H_f^{\circ}[C] - \left(\Delta H_f^{\circ}[A] + \Delta H_f^{\circ}[B]\right)$$
$$\Delta H^{\circ}_{reaction} = (1\text{mol})(523 \text{ kJ/mol}) - ((1\text{mol})(433 \text{ kJ/mol}) + (1\text{mol})(-256 \text{ kJ/mol}))$$
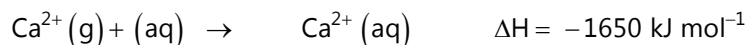
Since we have one mole of A, B and C, we multiply the standard enthalpy of formation of each reactant and product by 1 mole, which eliminates the mol denominator

$$\Delta H^{\circ}_{reaction} = 346 \text{ kJ}$$

We get the answer of 346 kJ, which is the standard enthalpy change of formation for the creation of variable "C".

Estimating enthalpies of solution from lattice enthalpies and hydration enthalpies

The hydration enthalpies for calcium and chloride ions are given by the equations:

$$Ca^{2+}(g) + (aq) \rightarrow Ca^{2+}(aq) \qquad \Delta H = -1650 \text{ kJ mol}^{-1}$$
$$Cl^{-}(g) + (aq) \rightarrow Cl^{-}(aq) \quad \Delta H = -364 \text{ kJ mol}^{-1}$$

The following cycle is for calcium chloride, and includes a lattice dissociation enthalpy of +2258 kJ mol-1. We have to use double the hydration enthalpy of the chloride ion because we are hydrating 2 moles of chloride ions. Make sure you understand exactly how the cycle works.
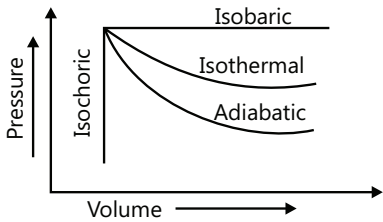

So,
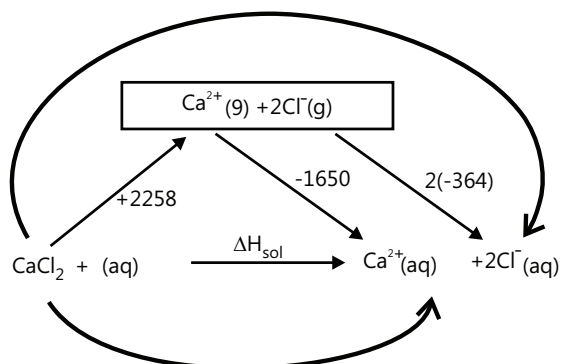
ΔHsol = +2258 - 1650 + 2(-364)

ΔHsol = -120 kJ mol-1

Whether an enthalpy of solution turns out to be negative or positive depends on the relative sizes of the lattice enthalpy and the hydration enthalpies. In this particular case, the negative hydration enthalpies more than made up for the positive lattice dissociation enthalpy.

POINTS TO REMEMBER

S. No	Terms	Description
1	System, surrounding and Boundary	A specified part of the universe which is under observation is called the system and the remaining portion of the universe which is not a part of the system is called the surroundings.
		The system and the surroundings can interact across the boundary.
2	Types of System	Open System $\Delta E \neq 0$, $\Delta m \neq 0$
		Closed System $\Delta E \neq 0$, $\Delta m = 0$
		Isolated System $\Delta E = 0$, $\Delta m = 0$
3	Thermodynamic Processes	**(a) Isothermal process** Occurs at constant temperature; $\Delta T = 0$
		(b) Adiabatic process Occurs without exchange of heat With surrounding, q = 0.
		(c) Isobaric process Occurs at constant pressure, $\Delta p = 0$
		(d) Isochoric process Occurs at constant pressure $\Delta V = 0$
4	Intensive and extensive properties	Those properties which do not depend on the mass of the sample are intensive properties whereas the others are extensive properties.
5	State Function	Those functions which do not depend on path followed during the change and depend only upon the initial and final state of the system.

S. No	Terms	Description
6	Sign Conventions for Heat and work	Heat absorbed by the system = q positive Heat evolved by the system = q negative Work done on the system = w positive Work done by the system = w negative
7	First law of Thermodynamics	First law of thermodynamics deals with the conservation of energy. $\Delta E = q + W$ Also, $\quad q = nC_v \Delta T$ In rev Isothermal Expansion of gas, $q = -W = P_{ext} \Delta V (\Delta E = 0)$ $q = -W = nRT \ln \dfrac{V_2}{V_1}$ In rev Isothermal Expansion of gas, $W = -q = -nC_v \Delta T = nC_v (T_1 - T_2)$ $pV^{\gamma} = $ constant, where $\gamma = \dfrac{C_p}{C_v}$ TV^{γ} constant and Also, In adiabatic rev process, $P^{1-\gamma}T^{\gamma} = $ constant
8	Graphical Representation of four Basic thermodynamic processes	Graphical representation of four basic thermodynamic Process.
9	Enthalpy (H)	$H = E + PV \Rightarrow dE + PdV + VdP$ At constant pressure $dH = dE + pdV \; (\because dP = 0) \; = Q_p = C_p \Delta T$
10	Entropy (S)	$S = \dfrac{q_{rev}}{T}; \; \Delta S = nC_v \ln\left(\dfrac{T_2}{T_1}\right) + nR \ln\left(\dfrac{V_2}{V_1}\right)$ $= nC_p \ln\left(\dfrac{T_2}{T_1}\right) + nR \ln\left(\dfrac{P_1}{P_2}\right)$
11	Gibbs Free Energy (G)	$G = H - TS \Rightarrow \Delta G = \Delta H - T\Delta S$ at constant temperature. Also, $dG = Vdp - SdT$ At constant temperature, $\Delta G = nRT \ln(P_2 / P_1)$
12	Criteria for Spontaneity	For a spontaneous process, entropy of universe must increase, i.e., $\Delta S_{univ} > 0$ or $\Delta G < 0$ (a) If $\Delta H < 0$ and $\Delta S > 0$, ΔG is always negative, always spontaneous. (b) If $\Delta H > 0$ and $\Delta S < 0$, ΔG is always positive, always non-spontaneous. (c) If $\Delta H > 0$ and $\Delta S > 0$, ΔG process will be spontaneous at higher temperature but non-spontaneous at lower temperature. (d) If $\Delta H < 0$ and $\Delta S < 0$, ΔG process will be spontaneous at Lower temperature but non-spontaneous at higher temperature.

S. No	Terms	Description
13	Standard Molar Enthalpy of formation $\left(\Delta H^0_{f_m}\right)$	It is the enthalpy change associated with the formation of one mole of a substance in the standard state from the constituent elements in their standard state. It can be either positive or negative.
14	Standard Molar Enthalpy of combustion $\left(\Delta H^0_{comb}\right)$	It is the heat evolved when one mole of a substance is the standard state is oxidized completely. (ΔH^0_{comb}) is always negative.
15	Standard Enthalpy reaction $\left(\Delta H^0_{rxn}\right)$	It is the net enthalpy change associate with a reaction. It is determined with the help of $\Delta H^0_{f_m}$ or ΔH^0_{comb} as $$\Delta H^0_{rxn} = \sum \Delta H^0_{f_m} \text{ (products)} - \sum \Delta H^0_{f_m} \text{ (reactants)} \text{ Or}$$ $$\Delta H^0_{rxn} = \sum \Delta H^0_{comb} \text{ (reactants)} - \sum \Delta H^0_{comb} \text{ (products)}$$ By convention ΔH^0_f of pure element is taken to be zero.
16	Calorimetry	If a reaction is carried out in a calorimeter, the enthalpy change of a reaction can be determined as $q = mS\Delta T$ Where, m = mass of calorimeter contend S = specific heat of calorimeter content $\Delta T = T_{final} - T_{initial} = $ change in temperature of calorimeter
17	Bond Dissociation Energy and Bond Enthalpy	Bond dissociation energy is the average energy required to break a specific type of bond in a molecule. **Bond enthalpy of a Compound**: It is the total energy required to convert one mole of gaseous substance into their constituent atoms. In term of bond-enthalpy, ΔH^0_{rxn} can be determined as $$\Delta H^0_{rxn} = \sum BE(\text{reactants}) - \sum BE(\text{products})$$
18	Resonance Energy	It is the energy released by the conjugated system due to delocalization of electrons. It is the difference in enthalpy change (between one determined Experimentally (calorimetrically) and other calculated Theoretically $\Rightarrow \Delta H \text{ (RE)} = \Delta H_{(exp)} - \Delta H_{(theo)}$
19	Enthalpy of Neutralization	It is the heat liberated when one gram equivalent of a strong acid or base is neutralized completely. Hence, all neutralization reactions are exothermic in nature.
20	Enthalpy of Hydration (ΔH^0_{hyd})	It is the heat evolved when one mole of a substance is hydrated to a certain specific degree of hydration, e.g, $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 + 5H_2O(s)$ En thalpy of hydration,
21	Lattice Energy (U_0)	**Lattice Energy** (U_0) It is the heat liberated when one mole of an ionic compound in its standard state is formed from ions in their gaseous state, e.g. $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$; $\Delta H - U_o$