

Thermodynamics: First Law, Calorimetry, Enthalpy

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CHEM 102H
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Calorimetry

- Reactions are usually done at either constant V (in a closed container) or constant P (open to the atmosphere).
- In either case, we can measure q by measuring a change in T (assuming we know heat capacities).

Calorimetry: constant volume

- $\Delta U = q + w$ and $w = -P_{\text{ex}}\Delta V$
- If V is constant, then $\Delta V = 0$, and $w = 0$.
- This leaves
$$\Delta U = q_v,$$
again, subscript v indicates const. volume.
- Measure ΔU by measuring heat released or taken up at constant volume.

Calorimetry Problem

- When 0.2000 g of quinone ($C_6H_4O_2$) is burned with excess oxygen in a bomb (constant volume) calorimeter, the temperature of the calorimeter increases by $3.26^\circ C$. The heat capacity of the calorimeter is known to be $1.56 \text{ kJ}/^\circ C$.
- Find ΔU for the combustion of 1 mole of quinone.

Calorimetry: Constant Pressure

- Reactions run in an open container will occur at constant P.
- Calorimetry done at constant pressure will measure heat: q_p .
- How does this relate to ΔU , etc.?

q_p & ΔU

- $\Delta U = q + w = q - P\Delta V$
- At constant V, $P\Delta V$ term was zero, giving $\Delta U = q_v$.
- If P is constant and $\Delta T \neq 0$, then $\Delta V \neq 0$.
 - In particular, if gases are involved, $PV = nRT$
- $w_p \neq 0$, so $\Delta U \neq q_p$

Enthalpy: A New State Function

- It would be nice to have a state function which is directly related to q_p :

$$\Delta(?) = q_p$$

- We could then measure this function by calorimetry at constant pressure.

- Call this function **enthalpy**, H , defined by:

$$H = U + PV$$

Enthalpy

- Enthalpy: $H = U + PV$

- U , P , V all state functions, so H must also be a state function.

- $\Delta H = q_p$?

– Do some algebra, assuming that P is constant:

- $\Delta H = \Delta U + \Delta(PV)$
 $= \Delta U + P\Delta V$

$\Delta H = q_p$

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V \\ &= (q + w) + P\Delta V\end{aligned}$$

But $w = -P\Delta V$, so:

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

And since we used constant P , this is

$$\Delta H = q_p$$

Compare ΔU & ΔH

$$\Delta H = \Delta U + P\Delta V \quad (\text{const. } P)$$

- $P\Delta V$ term due to expansion or compression.
 - For solids & liquids, $P\Delta V$ is small.
- Therefore, $\Delta H \approx \Delta U$ for condensed phase systems.
- For systems involving gases, ΔH and ΔU may differ considerably

ΔH for Physical Processes

$$\Delta H = \Delta U + P\Delta V \quad (\text{const. } P)$$

- If heat must be put in to the system to bring about a physical change, then $\Delta H > 0$ for that process.
 - For changes involving only condensed phases (solids & liquids), $P\Delta V$ contribution is small.
- ΔH for physical processes can be qualitatively understood by thinking about intermolecular forces.

Compare ΔU & ΔH ; Examples

- | | |
|--|--|
| <ul style="list-style-type: none">• A heat input of 6.004 kJ is required to melt one mole of ice at 1 atm. pressure. What is ΔH? What is ΔU? | <ul style="list-style-type: none">• A heat input of 40.62 kJ is required to boil one mole of water at 1 atm. pressure. What is ΔH? What is ΔU? |
|--|--|

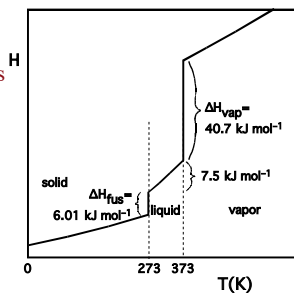
Conclusion from example

- If volume changes are large, the difference between ΔH and ΔU can be significant.
- Volume changes are 'large' when the number of moles of gas changes from the initial and final states.
- Since gases usually are approximately ideal, $\Delta(PV) \approx \Delta(nRT) = (\Delta n)RT$, so...

$$\Delta H = \Delta U + \Delta(PV) \approx \Delta U + (\Delta n)RT$$

Heating curves (H₂O shown)

- Melting and Boiling constitute "jumps" in the heating of a substance – their sizes reflect strength of intermolecular forces overcome in the processes.
- All phase transitions occur at constant temperatures.



Again, Heat Capacities...

- For one mole of an ideal gas: $U = \frac{3}{2} RT$
- We've seen that $\Delta U = q_v$, therefore

$$\text{since } C_v = \frac{q_v}{\Delta T}, C_v = \frac{\Delta U}{\Delta T} \left(= \frac{dU}{dT} \text{ in the limit} \right)$$

$$C_v = \frac{3}{2} R \text{ for an ideal gas}$$

- We've seen that $\Delta H = q_p$, and $\Delta H = \Delta(U + PV)$

$$\text{since } C_p = \frac{q_p}{\Delta T}, C_p = \frac{\Delta H}{\Delta T} \left(= \frac{dH}{dT} \text{ in the limit} \right)$$

$$C_p = \frac{3}{2} R + \frac{d(PV)}{dT} = \frac{3}{2} R + \frac{d(RT)}{dT} = \frac{5}{2} R \text{ for an ideal gas}$$

Enthalpy & Chemistry

- Many reactions occur at constant P, so ΔH is a useful quantity.
- $\Delta H < 0 \rightarrow$ heat is released, so reaction is exothermic
- $\Delta H > 0 \rightarrow$ heat is absorbed, so reaction is endothermic
- ΔH is related to the amount of energy we might get out of a reaction.

H vs. ΔH

- We always talk about ΔH , never H itself. (Same is true for U & ΔU)
Why?
- H is an energy, so we need some reference point. "Absolute energy" is not readily defined.

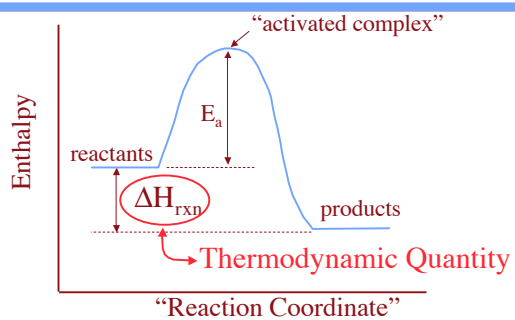
Reaction Enthalpies

- Enthalpies don't just apply to changes in physical state, but to reactions too. Example:
$$\text{Fe}(s) + 2\text{S}(s) \rightarrow \text{FeS}_2(s) \quad \Delta H^\circ = -178.2 \text{ kJ}$$
- If these chemicals constitute the "system", then when the reaction occurs, 178.2 kJ of heat will be released into the surroundings if 1.0 mol of FeS_2 is formed.
- Note: this says nothing about the rate of the reaction or the conditions under which it would be practical to carry it out.

Reaction Enthalpy

- * If $\Delta H_{\text{reaction}}$ is negative, energy is given off.
 - “Exothermic”
- * If $\Delta H_{\text{reaction}}$ is positive, energy is absorbed.
 - “Endothermic”
- * We can NOT predict whether a reaction will occur based only on ΔH !

Energy Diagram



Using Bond Enthalpies

- * Imagine running the reaction as follows:
 - break every bond in reactants, giving a collection of atoms
 - make new bonds among these atoms to form products

reactants \rightarrow free atoms \rightarrow products
- * Will each step cost energy, or release energy?

Standard States

- Define a “standard state:”
The enthalpy of an element in its most stable physical form at 1 atm and 25°C is equal to zero.
- Gives a reference for each element, since they are not interconverted in chemical processes
- This definition fixes all ΔH values, since H is a state function.

Tabulating & Using ΔH

- Exhaustive tabulation of ΔH 's (for all possible reactions) is not feasible.
- Exploit the fact that ΔH is a state function to get maximum useful information from a more reasonable amount of data.
- “Standard Enthalpy of Formation,” ΔH_f°

Formation Reactions

- For any compound we can write a “formation reaction” in which:
$$\text{Elements in standard states} \longrightarrow \text{1 mole of compound}$$
- ΔH for such a reaction is called the “standard enthalpy of formation,” ΔH_f° , for the compound.
- Also called “heat of formation”

Formation Reactions

Elements in standard states \longrightarrow *1 mole of compound*



- * Always one mole of product, so often need to use fractional coefficients.
- * Many such reactions can not actually be carried out. (But values can be found indirectly & tabulated.)

Using ΔH_f° 's



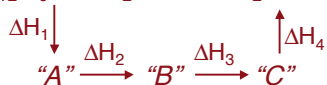
- * $\Delta H = ?$
- * Since H is a state function, we can create any # of intermediate states.
- * Use ΔH for these steps to find the ΔH we want.

“Path Independence”

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

- * This does not specify what might exist between reactants and products.
- * ΔU is “path independent.” We can imagine any set of steps that get us from the reactants to the products.
- * Because it is path independent, we say ΔH is a “state function.”

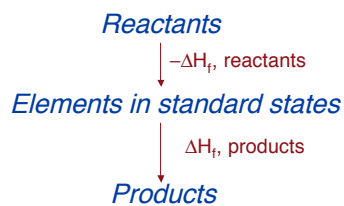
H is a state function!



- Because H is a state function:
 $\Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$
- $\Delta H_1, \Delta H_2$, etc. refer to the individual steps

Using ΔH_f° 's to find ΔH_{rxn}

- Choose a useful path for the reaction.



$$\Delta H_{\text{rxn}} = \Delta H_f \text{, products} - \Delta H_f \text{, reactants}$$

Problem

- Given the ΔH_f° 's below, find ΔH for the combustion of one mole of glucose at 298 K.



(Data are from Appendix 2 in your book.)

Hess's Law

- For any reaction, we can write:
$$\Delta H_{\text{rxn}} = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$$
- n's are the stoichiometric coefficients from the balanced chemical equation.
- This lets us find ΔH for any reaction from a table of ΔH_f° 's.

Another Problem - Hess's Law

- Acetylene torches are used in welding.
Chemical reaction involved is:
$$\text{C}_2\text{H}_2(\text{g}) + 5/2 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$$
- Find ΔH° for this reaction.
- Estimate the maximum temperature which could be obtained in an acetylene flame.
- Some useful data are on the next slide.

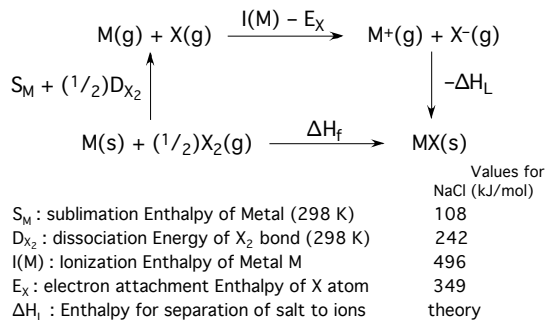
Data For Problem

- Heat of formation (ΔH_f°)

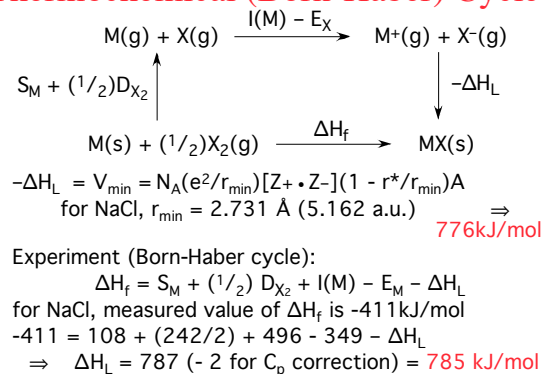
$\text{C}_2\text{H}_2(\text{g})$	226.73 kJ/mol
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{g})$	-241.8
- Heat capacities (C_p)

$\text{C}_2\text{H}_2(\text{g})$	44 J/mol K
$\text{CO}_2(\text{g})$	37
$\text{H}_2\text{O}(\text{g})$	36

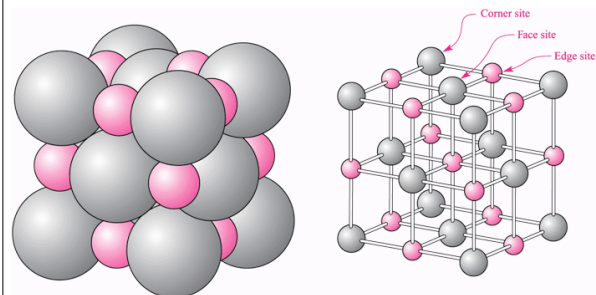
Thermochemical (Born-Haber) Cycle



Thermochemical (Born-Haber) Cycle



Rocksalt (NaCl) type: ccp stacked Cl; all octahedral holes filled



Ionic Bonding; Lattice Energies

Energy

Lattice Energies - Details

$V = V_{\text{Coulomb}} + V_{\text{repulsion}}$

ion - ion Coulomb interactions repulsions between ion cores

eg., NaCl-type: (cgs units - a factor of $1/4\pi\epsilon_0$ must be included to convert to SI)

$V_{\text{Coulomb}} = +6 (e^2/r)Z_+ \cdot Z_- + 12 (e^2/\sqrt{2}r)(Z_+)^2 + 8 (e^2/\sqrt{3}r)Z_+ \cdot Z_- + 6 (e^2/2r)(Z_+)^2 + \dots$

NaCl-type:

$V_{\text{Coulomb}} = N_A(e^2/r)[Z_+ \cdot Z_-] \times A$ $A = [-6 + 12/\sqrt{2} - 8/\sqrt{3} + 6/2 - 24/\sqrt{5} + \dots]$

The Madelung constant: a geometrical parameter that is the same for all compounds of a given structure type

Ion core — Ion core repulsions

♦ $V_{\text{repulsion}} = + N_A C \exp\{-r/r^*\}$
 estimated from compressibilities, r^* is always much smaller than a typical internuclear distance ($\sim 0.345 \text{ \AA}$).

Alternative:
 $V_{\text{rep}} = + N_A (B/r^n)$

ion core	n
He	5
Ne	7
Ar	9
Kr	10
Xe	12

$V = N_A(e^2/r)[Z_+ \cdot Z_-]A + N_A C \exp\{-r/r^*\}$

Minimize (set $(dV/dr) = 0$) to obtain:

$C \exp\{-r_{\text{min}}/r^*\} = - e^2 [Z_+ \cdot Z_-] A r^*/(r_{\text{min}})^2$

$V_{\text{min}} = N_A(e^2/r_{\text{min}})[Z_+ \cdot Z_-](1 - r^*/r_{\text{min}})A$

$V_{\text{min}} = N_A(e^2/r_{\text{min}}) \cdot [Z_+ \cdot Z_-](1 - 1/n)A$

Bond Enthalpies and Reactions

- We can measure the strength and length of chemical bonds. (some easily, some with great difficulty)
- Energy of a particular type of bond (carbon - hydrogen, etc.) approximately (but not exactly) the same in different molecules.
- This is because bonds are often mainly localized and because orbitals used to make bonds are similar in different molecules.

Using Bond Enthalpies: Reaction Energy

- * Average bond enthalpies are tabulated.
- * We can use these to *estimate* the enthalpy change for any chemical reaction for which bond enthalpies are known.
- * Decide whether the reaction was likely to succeed, evaluate possible fuels, etc.

Reaction Enthalpy

Reactants → Products

Reaction Enthalpy: Enthalpy taken in or given off during reaction

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Using Bond Energies

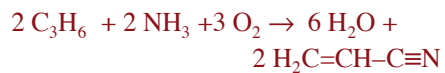
- * Can use bond energies to find the energy required or released in these imaginary steps. Get ΔH by combining these.

- * $\Delta H_{\text{reaction}} = \sum \text{BE}_{\text{reactants}} - \sum \text{BE}_{\text{products}}$

(“ Σ ” means “summation”)

NOTE: Because bond energies are defined relative to ATOM energies, this has a “reactants” minus “products” - not usual!

Acrylonitrile Synthesis



- Use bond enthalpies to estimate ΔH for this reaction. Some data are on next slide.

Some Bond Enthalpies (kJ/mol)

- Diatomic molecules (actual values)

H—H 432.0 O=O 493.6

C≡O 1071

- Other bonds (avg. values)

C—C 348 C=C 612 C≡C 837

C—H 412 C=N 615 C≡N 890

N—H 388 N=O 630

O—H 463

Thermodynamics & Chemistry

- Study of the energy changes associated with chemical or physical processes.
- Chemical applications of principles you will study in physics & engineering
 - reaction energy, fuels, etc.
- Goal - to be able to predict whether or not a given reaction can occur, using simple tabulated data.

Thermodynamics vs. Kinetics

- * Thermodynamics tells us things about the eventual outcome of a chemical reaction, but NOT about how fast the reaction might be.
- * To know if something will happen fast, we need to consider kinetics.
- ☛ Need both thermodynamics and kinetics to assess practical usefulness of a reaction.
