12 • Chemical Thermodynamics
Commonly Used Terms
(1 of 12)

thermodynamics	Study of NRG changes & flow of NRG. Tells whether a reaction is possible.
system	That portion of the universe on which we focus.
surroundings	Everything outside the system.
adiabatic	A change without heat transfer between the system and its surroundings.
isothermal	A change that occurs at constant temperature.
state functions	Properties that depend on the initial and final state, not on how the change was made. ex: ΔH, temp, but not work

12 • Chemical Thermodynamics
Heat Capacity and Specific Heat
(2 of 12)

Energy changes can be measured using **calorimetry**. Often this involves heating water under controlled conditions (a bomb calorimeter).

Three closely related terms are:
heat capacity is the amount of heat needed to change a system by 1°C.
molar heat capacity is the amount of heat needed to change a mole of a substance by 1°C.
specific heat is the amount of heat needed to change 1 gram of a substance by 1°C. (Water: 1 cal/g°C = 4.184 J/g°C)

Note that heat capacity is an extensive property whereas the other two are intensive.

12 • Chemical Thermodynamics
First Law of Thermodynamics
(3 of 12)

The **first law**: "if a system undergoes some series of changes that ultimately brings it back to its **original** state, the net energy change is **zero**."

$\Delta E = E_{final} - E_{initial}$ $\qquad \Delta E = 0$ when $E_{final} = E_{initial}$

The **usefulness** of this idea is that the internal energy, ΔE, depends only on the initial and final state, not on how you get there. Every path you take from $E_{initial}$ to E_{final} takes the same amount of energy. (no perpetual motion)

There are two ways for a system to exchange energy with the surroundings, **heat** and **work**. $\qquad \Delta E = q - w$
[q = heat absorbed **by** system, w = work done **by** system]

12 • Chemical Thermodynamics
Work and PV Work
(4 of 12)

From physics, **work = force $\times$ distance = F $\times$ d**.
In chemistry there is **electrical** work (e-'s through a wire) and **P∆V** work as a gas expands.

Use pressure = force/area and area $\times$ distance = volume to derive **work = P∆V** from **work = F ⋅ d**.

Note that units of work are units of energy. Energy and work are two forms of energy. **Doing work** on a system **increases the potential ene**rgy of the system.

P∆V work is in **L⋅atm** $\qquad$ 1 L⋅atm = 24.2 cal = 101.3 J

PV = nRT… work can be calculated as **work = ∆nRT** for chemical reactions where the # of moles of gas change, ∆n.

12 • Chemical Thermodynamics
Work is NOT a State Function
(It depends on HOW you do the work.)
(5 of 12)

Q: Gas in a piston at a pressure of 10 atm is allowed to expand from 1 L to 10 L. How much work done?

A: It depends on the resisting force.

If it expands against 0 atm pressure,

$$P\Delta V = 0 \text{ atm} \times 9 \text{ L} = \textbf{0 L·atm}$$

Expanding against 1 atm pressure, V_{final} is 10 L

$$P\Delta V = 1 \text{ atm} \times 9 \text{ L} = \textbf{9 L·atm}$$

Expanding in **two** steps, first, against 2 atm, $V_{final} = 5$ L

$$P\Delta V = 2 \times 4 \text{ L} = 8 \text{ L·atm}$$

then in a second step against 1 atm, $V_{final} = 10$ L

$$P\Delta V = 1 \times 5 \text{ L} = 5 \text{ L·atm} \dots \text{ Total} = \textbf{13 L·atm}$$

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12 • Chemical Thermodynamics
Reversible Processes
(6 of 12)

From the PΔV work example, you can see that the more steps (and smaller increments) you use to get the work from the system, the more work you can get.

There is an upper limit to how much work can be derived from any system. That maximum work is called the Gibb's Free Energy, ΔG.

The theoretical maximum work can be achieved if the steps are so small that they can go either way, if they are **reversible**.

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12 • Chemical Thermodynamics
$\Delta H = \Delta E + P\Delta V$
(7 of 12)

If a chemical reaction occurs in a **closed** container $\Delta V = 0$ and so $P\Delta V$ **work $= 0$**. $\Delta E = q - w$ becomes $\Delta E = q$.

In a system at **constant pressure** (a common situation) the energy change involves both heat (q) & work (PΔV).
$\Delta E = q - P\Delta V$ [PΔV = work done BY the system] or
$q = \Delta E + P\Delta V$ q at constant pressure is called ΔH.
$\Delta H = \Delta E + P\Delta V$ or $\Delta E = \Delta H - P\Delta V$

The work (PΔV) is generally insignificant unless the # of moles of **gas** ($\Delta n = n_{final} - n_{initial}$) is changing. $P\Delta V = \Delta nRT$

Recall that if Δn is negative (# moles decreasing) work is negative (work is being done ON the system).

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12 • Chemical Thermodynamics
Hess's Law of Heat Summation
(8 of 12)

If several reactions add up to give an overall reaction, the ΔH**'s** of the reactions will add up to the overall ΔH.

Standard Heats of Formation, ΔH_f°, are useful for this purpose. This is the energy involved in making a mole of a substance from its elements at 25°C and 1 atm pressure.

This law is often written as:

$$\Delta H^\circ_{reaction} = \Sigma \Delta H_f^\circ_{products} - \Sigma \Delta H_f^\circ_{reactants}$$

Note: ΔH_f° for elements is 0.

If you are NOT using heats of formation, you need to write out the equations to see how they combine.

12 • Chemical Thermodynamics
Bond Energies
(9 of 12)

Bond energy is the amount of energy needed to BREAK a certain bond.

You can determine the approximate energy change in a chemical reaction by summing the bond energies of the reactants and subtracting the bond energies of the products.

Note: this is opposite to the Hess's Law (products - reactants) because bond energy involves **breaking** bonds whereas $\Delta H°_f$ involve **forming** bonds.

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12 • Chemical Thermodynamics
Two Big Driving Forces of the Universe
Enthalpy (ΔH) and Entropy (ΔS)
(10 of 12)

Things in the world tend toward lowest energy ($-\Delta H$) and also tend toward greatest disorder ($+\Delta S$).

More disorder can be recognized as:
- greater # of moles of gas formed
- gas > liquid > solid and (aq) > (s)
- greater volume formed
- mixed molecules (HI) formed from diatomic molecules
  example: $H_2(g) + I_2(g) \rightarrow 2HI(g)$ $+\Delta S$

Note: $\Delta S°$ can be calculated using Hess's Law, but $S°$ of elements is NOT 0. Also, $S°$ is often reported in J/mol·K and cal/mol·K, not **k**J and **k**cal… watch your units!

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12 • Chemical Thermodynamics
The Second Law of Thermodynamics
$\Delta G = \Delta H - T\Delta S$
(11 of 12)

The second law defines a value called Gibb's Free Energy symbolized as ΔG. This represents the theoretical maximum work that can be done by a system.

A reaction is spontaneous when ΔG is negative ($\Delta G<0$). The reverse reaction is spontaneous when ΔG is positive. When $\Delta G = 0$, the reaction is at equilibrium.

ΔH	ΔS	Spontaneous…
—	+	… at all temperatures
—	—	… at LOW temperatures
+	+	… at HIGH temperatures
+	—	the **reverse** reaction is spontaneous

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12 • Chemical Thermodynamics
ΔG (thermodynamics) and K_{eq} (equilibrium)
(12 of 12)

We have been calculating $\Delta G°$ values, that is, ΔG under **standard** conditions. Once a reaction begins, the concentrations **change** and the value of ΔG is **different**.

If $\Delta G° < 0$, then the reaction will proceed in a **forward** direction. As it does, however, the value of ΔG will **increase** until the forward and reverse reactions are balanced and $\Delta G = 0$. This is called **equilibrium**.

If $\Delta G° > 0$, then the **reverse** reaction will proceed and the value of ΔG will **decrease** until equilibrium is reached.

$\Delta G°$ gives information about where we are **in relation to equilibrium**. There is a formula that combines ΔG and **Keq**.