## ASSIGNED READINGS:

**TODAY'S CLASS:**   finish Ch.6…
                              start Ch. 19.1-19.5

*Remember:  Chem 101 seminars this week*

(1)

## What we want to predict is:      <u>Spontaneity</u>

**Spontaneous**:  *adj*  Webster's dictionary
    **Developing without apparent external influence, force, cause or treatment**

   CHEMISTRY:  occurring without outside intervention

▪ implies ONLY that it is energetically favourable for the process to occur,  IN A SPECIFIC DIRECTION !

▪ **does NOT imply anything about a process's speed**

> **Sometimes direction of spontaneity is easy to predict:**
> • Fall off cliff  *vs.*  Fly to top
> • Heat flows FROM hot object TO cold object
> • Ice melts at temperatures > 0°C

(2)

## CHAPTER 19  Entropy & Free Energy
*(we'll cover this in less detail than text:  focus on lecture material)*

**For now:  we'll cover these:**

*General comprehension:*
19.1  Spontaneous change
       & equilibrium
19.2  Heat and spontaneity
19.3  Dispersal of energy & matter
19.4  Entropy & the 2nd law

*In detail:*
**19.5  Entropy changes & spontaneity**
**19.6  Gibbs Free Energy**

**Chapter Goals:**
- Understand the concept of entropy and how it relates to spontaneity
- Predict whether a process is product- or reactant favoured (proceeds forward vs. reverse)
- Use tables of data in thermodynamic calculations
- Define and use a new thermodynamic function:
        Free Energy

(3)

## 19.1-19.2  Spontaneous change leads to equilibrium, but is not dependent upon heat flow…

Spontaneous processes:
- occur without outside intervention
- *net change of system stops* once system reaches a state of *equilibrium (more detail later…)*
  → *e.g.,* heat flows from warmer object to colder… until objects both at same temperature

Exothermic processes are OFTEN spontaneous…BUT:

Thermoneutral (no heat flow) processes CAN be spontaneous:
- gas flowing into an evacuated chamber…or leaking out of a balloon

Endothermic processes CAN be spontaneous:
- ice melts at T > 0°C, but not T < 0°C (but it's always endothermic!)
- $NH_4Cl$ dissolves in water (but causes the water to cool down a lot…)

(4)      **Temperature seems important.  WHY???**

## 19.3 Dispersal of energy & matter *(extra detail in text)*

WHAT DRIVES CHEMICAL PROCESSES?

1.) **dispersal of matter**
 → increasing the randomness of the universe
  by breaking large particles into many smaller ones, *OR*
  by spreading matter out over larger volumes

2.) **dispersal of energy**
 → distributing energy over as many particles of
  matter as possible
  via heat flow: transfer of kinetic energy between particles

A process **WILL** be spontaneous if:  energy & matter *BOTH* dispersed
A process **MIGHT** spontaneous if:   energy *OR* matter is dispersed
A process will **NOT** spontaneous if: *neither* E *NOR* matter is dispersed

(5)   → **NOTICE: "dispersal" = creating disorder**


## 19.4-19.5  Spontaneous Processes & Entropy

**Entropy (S)** = **DISORDER**   Units: J/K

→ A thermodynamic state function

→ A LITTLE UNUSUAL:
  Magnitude depends strongly on temperature

  MAKES SENSE WHEN YOU CONSIDER:
  particles moving faster at higher temp…
  mixing around with each other…
  → MORE DISORDERED

⇨ *Entropy itself is NOT a type of energy*

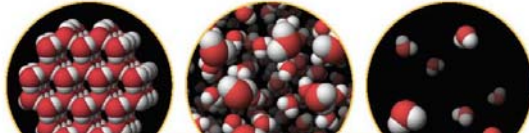  *however: if multiply entropy by temperature: i.e., SxT
    can think about how much energy is being spent on
     "making a mess"*

(6)

DISORDER can be estimated:  "positional entropy"    *(more details? 19.3)*
  How hard is it to "find" a particle?

▪ How many different places can each of the substance's particles be inside system?



solid  →  liquid  →  gas
low disorder                high disorder

▪ Possible to statistically calculate entropy...
  Chem 206:  focus on logic only

CHALLENGE:  Estimate ΔS (sign...) for phase changes

| | | |
|---|---|---|
| Sublimation: | Evaporation: | Condensation: |
| Deposition: | Fusion: | Solidification: |

(7)

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**Second Law of thermodynamics:  *"mess happens"***

2nd LAW:  In any spontaneous process, the total disorder of the **universe** (= system + surroundings) increases.

*Mathematically:  NET entropy increase...*
  SPONTANEOUS  IF:   $\Delta S_{univ} = (\Delta S_{sys} + \Delta S_{surr}) > 0$

Another version of the 2nd law:

  THE ENTROPY OF THE UNIVERSE IS INCREASING...

Ominous:  energy tends to be converted from useful forms
    **(potential E we can harness to do work or generating
    heat where we need it)** into heat in the surroundings
    **(which corresponds to increased disorder...)**

(8)

## Determining entropy changes during processes (19.4)

**1.) CAN ESTIMATE: USING LOGIC**
- MORE GASES → huge increase in disorder → $\Delta S_{sys} > 0$
  *e.g.,* burning glucose OR exploding nitroglycerin

- If more molecules (of any kind): more disorder!

  *& of course the opposites are also true...*

**2.) CAN CALCULATE: USING HESS'S LAW**
- tabulated data: standard entropies of formation, $S^o_f$
  = entropy gained when convert substance from
  perfect crystal at T = 0 K to std. state conditions

- NOTE: "Δ" not used with $S^o_f$ values
  → **values relative to *perfect order (S = 0) at absolute zero***
     → perfect crystalline solids: no defects
     → at 0 K: no thermal energy ∴ no movement
        ***(this is the 3rd law of thermodynamics)***

(9)

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## Sodium reacts with chlorine... $2Na(s) + Cl_2(g) \rightarrow NaCl(s)$

<u>Rationalize</u>: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$ using: ① **logic &**
                                                                   ② **calculations**

**A.) First consider system:**
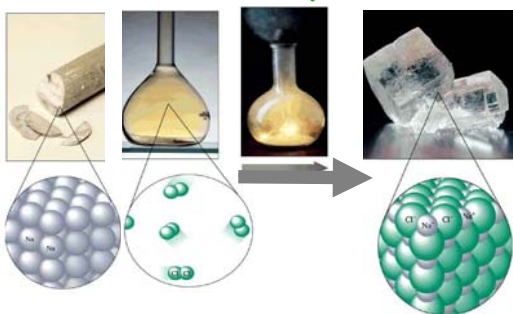


|  | $S^o_f$ |
|---|---|
| **Na(s)** | 51.21 J/K·mol |
| **Cl$_2$(g)** | 223.08 J/K·mol |
| **NaCl(s)** | 72.11 J/K·mol |

① **PREDICT VIA LOGIC:**
  $\Delta S_{sys}$

② **Hess' law:** $\Delta S^o_{rxn} = \sum S^o_f(\text{products}) - \sum S^o_f(\text{reactants})$

(10)

## B.) Now consider surroundings:
### is heat transferred to/from system?

**IF exothermic reaction occurs in system:** $\Delta S_{surr} > 0$



← surroundings initially cooler, but now hotter →

**IF endothermic reaction occurs in system:** $\Delta S_{surr} < 0$



← surroundings initially warmer, but now cooler →

The E responsible for changing the disorder of **surroundings** = $\Delta S^{\circ}_{surr} \times T$ is the thermal energy exchanged because of **heat flow to/from system**

**THUS:** $\quad \Delta S^{\circ}_{surr} = \dfrac{-\Delta H^{\circ}_{sys}}{T} \quad$ *assuming constant P conditions...*

(11)

Na & $Cl_2$ spontaneously react, but system's entropy ↓
IMPLIES: entropy of rest of universe must INCREASE
For this rxn: $\left|\Delta S_{surr}\right| > \left|\Delta S_{sys}\right|$ causes $\Delta S_{univ} > 0$ ...

Observation of reaction:
- **HIGHLY EXOTHERMIC**
  $\Delta H_{rxn} < 0$, so $q_{surr} > 0$



⇨ **LOGIC:** $\Delta S_{surr} > 0$
surroundings now more disordered, because temp. ↑

**SO:** $\Delta S^{\circ}_{surr} = \dfrac{-\Delta H^{\circ}_{sys}}{T}$ & $\Delta H^{\circ}_{rxn}$ = **-411.12 kJ/mol NaCl(s)**
*let's assume we're at room temp.*

$= -(-411\ 120\ \text{J/mol})/(298\ \text{K})$
$= 1379.6\ \text{J/mol·K}$ ⇨ **Quantitative confirmation: Surroundings much more disordered**

So, do our calculations say rxn should be spontaneous?

## So…  WHAT DRIVES CHEMICAL PROCESSES?

1.)  increasing randomness of system…  **ENTROPY CHANGE OF SYSTEM**

2.)  increasing randomness of surroundings…
   …by ↑ thermal motion
   if heat flows out of system  **ENTHALPY CHANGE OF SYSTEM**

Overall:  will be able to determine net effect on universe.

Process SPONTANEOUS if universe becomes more disordered.

(13)

## The 2$^{nd}$ Law governs spontaneity
### & reveals net "driving force"

For a spontaneous process:
**(forward reaction occurs on its own)**    $\Delta S^{o}_{univ} > 0$

For a system at equilibrium:
**(no net change in either direction)**    $\Delta S^{o}_{univ} = 0$

For a non-spontaneous process:
**(reverse reaction occurs on its own)**    $\Delta S^{o}_{univ} < 0$

**The net driving force for a process is determined by:**

**Two quantifiable state functions of the SYSTEM:**
1) **ENTROPY:**    $\Delta S^{o}_{sys}$          ⇨ matter dispersal in sys.
2) **ENTHALPY:**   $\Delta H^{o}_{sys} = -T\Delta S^{o}_{surr}$  ⇨ matter dispersal in surr.

(14)        *…and now:  convert to the chemist's typical viewpoint…*

## ASSIGNED READINGS:

**BEFORE NEXT CLASS:**

**Read:**   rest of Ch.6, plus Ch.19 up to 19.5

   **+ WORK ON Problems from Ch.6 & 19**

**Next class:**   Ch. 19.6, 19.8, start Ch.13.1-13.5…

(15)