

Miscellaneous Notes



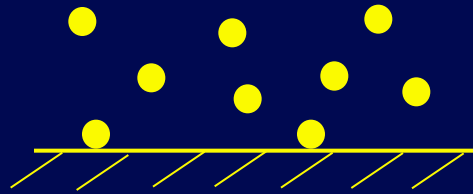
- The end is near – don't get behind.
- The PHYS 213 final exam times are
 - * 8-10 AM, Friday, Dec. 13
 - * 8-10 AM, Wednesday, Dec. 18

Homework 6 is due Tuesday, Dec. 10 at 8 am. (NO late turn-in).

- Course Survey = 2 bonus points (accessible in ByteShelf, but not until Dec. 4)

Lecture 19:

Surfaces, and Phase Transitions



Reading for this Lecture:
Elements Ch 13

Phase Transitions

Roadmap:

We'll start by looking at a simple model of atoms on surfaces, and discover that, depending on the temperature, the atoms prefer to be bound or to be flying free.

This is related to the common observation that materials can be found in distinct phases: E.g., solid, liquid, gas.

We'll learn how equilibria between these phases work.

Then we'll go back and try to understand why distinct phases exist in the first place.

Applications of Surface Chemistry

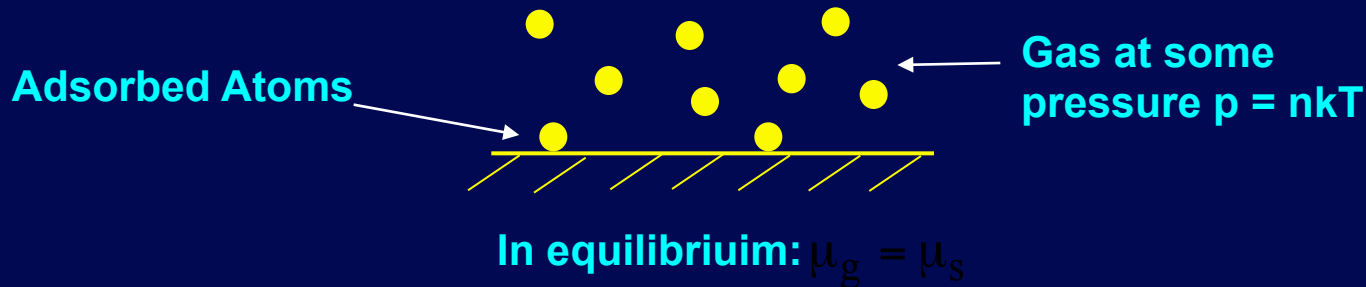
Catalysis -- purify engine exhaust

Oxidation of surfaces

Fabrication of high quality films

Binding of O₂ gas to hemoglobin and myoglobin in your body

.....



Chemical potential of the gas:

$$\mu_g = kT \ln \left(\frac{n}{n_Q} \right) = kT \ln \left(\frac{nkT}{n_Q kT} \right) = kT \ln \left(\frac{p}{p_Q} \right)$$

where we've defined

$$p_Q \equiv n_Q kT$$

p_Q , the “quantum pressure”, is the pressure it would take (hypothetically) to compress an ideal gas to the quantum density, so that there was 1 particle per “quantum cell”.

Chemical potential of the surface:

$$\mu_s = \frac{dF_s}{dN_s} \quad \text{with} \quad F_s = U_s - TS_s = ?$$

Adsorption of Atoms on a Surface



$$F_s = U_s - TS_s = -N_s \Delta - kT \ln(\Omega)$$

$$\Omega = \frac{M!}{(M - N_s)! N_s!}$$

Calculate the chemical potentials:

Bound atoms:

$$\frac{d(\ln \Omega)}{dN_s} = \ln \left(\frac{M - N_s}{N_s} \right), \text{ using } \frac{d(\ln N!)}{dN} = \ln N$$

$$\mu_s = \frac{dF_s}{dN_s} = -\Delta - kT \ln \left(\frac{M - N_s}{N_s} \right)$$

Equilibrium:

$$\mu_s = \mu_g \Rightarrow \frac{M - N_s}{N_s} = \frac{p_Q}{p} e^{-\Delta / kT}$$

M = # (single occupancy) binding sites on the surface

Δ = binding energy of an atom on site

N_s = number of bound atoms

F_s = Free energy of bound atoms

Atoms in the gas:

$$\mu_g = kT \ln \left(\frac{p}{p_Q} \right), \text{ where } p_Q = n_Q kT$$

We could solve this equation for N_s , but ...

Adsorption of Atoms (2)

... usually we want to know what fraction of the surface sites are occupied, for a given gas pressure p and temperature T :

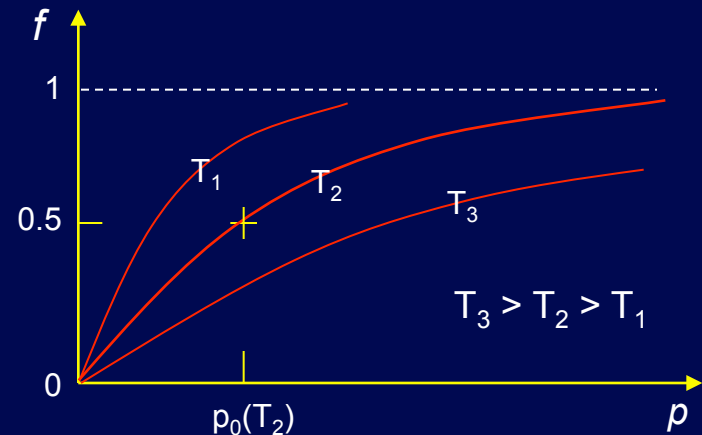
Using our result: $\frac{M - N_s}{N_s} = \frac{p_Q}{p} e^{-\Delta/kT} = \frac{p_0}{p}$, where $p_0 \equiv p_Q e^{-\Delta/kT}$

We obtain a simple relation for the fraction of occupied sites:

$$f \equiv \frac{N_s}{M} = \frac{p}{p + p_0}$$

More atoms go onto the surface at high pressure, because μ_{gas} increases with pressure.

$p_0(T)$ is the characteristic pressure at which half the surface sites are occupied. It increases with temperature due to the Boltzmann factor.



Example: Adsorption of Atoms

At $T = 300 \text{ K}$ and $p = 1 \text{ atm}$, it is observed that 50% of the binding sites on a particular metal surface are occupied. When the temperature is raised to 320 K at constant pressure, only 25% of the sites are occupied. (You may assume that p_Q is constant over this small temperature range.)

What is the binding energy of a site on the surface?

$$k = 8.617 \times 10^{-5} \text{ eV/K}$$

Solution

At $T = 300 \text{ K}$ and $p = 1 \text{ atm}$, it is observed that 50% of the binding sites on a particular metal surface are occupied. When the temperature is raised to 320 K at constant pressure, only 25% of the sites are occupied. (You may assume that p_Q is constant over this small temperature range.)

What is the binding energy of a site on the surface?

$$k = 8.617 \times 10^{-5} \text{ eV/K}$$

$$f(300\text{K}) = \frac{1}{2} = \frac{1 \text{ Atm}}{1 \text{ Atm} + p_0(300\text{K})} \rightarrow$$

$$p_0(300\text{K}) = 1 \text{ Atm} = p_Q e^{-\Delta/k(300\text{K})}$$

What is $p_0(320\text{K})$?

$$p_0(320\text{K}) = 3 \text{ Atm} = p_Q e^{-\Delta/k(320\text{K})}$$

So :

$$3 = e^{-(\Delta/k)(1/320 - 1/300)}$$

$$\Delta = k \ln(3) / (1/300 - 1/320) = 0.454 \text{ eV}$$

Act 1: Adsorption

1) At 10 atm, half the sites are occupied. What fraction are occupied at 0.1 atm?

- A) 1% B) 11% C) 90%

2) Keep the pressure constant, but increase T . What happens to f ?

- A) Decrease B) No effect C) Increase

Solution

1) At 10 atm, half the sites are occupied. What fraction are occupied at 0.1 atm?

A) 1%

B) 11%

C) 90%

$$f = \frac{p}{p + p_0} = \frac{0.1}{0.1 + 10} = 9.9 \times 10^{-3} \approx 1\%$$

At lower pressure, gas atoms hit the surface less often.

2) Keep the pressure constant, but increase T. What happens to f?

A) Decrease

B) No effect

C) Increase

Solution

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At lower pressure, gas atoms hit the surface less often.

2) Keep the pressure constant, but increase T. What happens to f?

A) Decrease

B) No effect

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Higher T:

⇒ higher p_Q and $e^{-\Delta/kT}$

⇒ p_0 increases

⇒ f decreases

$$p_0 \equiv p_Q e^{-\Delta/kT}$$

Makes sense? More atoms have enough thermal energy to leave.

Example: Oxygen in blood

Your body needs to carry O_2 from the lungs out to tissues (called T in the reactions below), using some carrier molecule. Suppose it's myoglobin. If there are M myoglobin binding sites and N_B bound oxygen molecules, (and Δ is the binding energy of oxygen to myoglobin), we can analyze the transport of oxygen from lungs to tissues.

Facts: $p_{O_2, \text{lungs}} = p_{O_2 @ \text{STP}} = 0.2 \text{ atm}$; $p_{O_2, \text{tissue}} = 0.05 \text{ atm}$; $f(\text{lungs}) = 2/3$

Solution

First look at the lungs. Ignore the effect of the oxygen on the myoglobin to which it binds, so it's just like the problem of adsorption by surface sites.

Equilibrium is described by: $\mu_{\text{gas}} = \mu_{\text{bound}}$.

The fraction of occupied myoglobin sites is: $f = \frac{N_B}{M} = \frac{p_{\text{O}_2}}{p_{\text{O}_2} + p_0}$

We can't calculate p_0 , but we know empirically that $f \approx 2/3$ in the lungs (where $p_{\text{O}_2} = p_{\text{lungs}} \approx 0.19 \text{ atm}$). That is, $p_0 \approx \frac{1}{2} p_{\text{lungs}}$

What happens in the tissue? p_0 is the same.

Empirically, $f \approx 1/3$, so $p_{\text{tissue}} \approx \frac{1}{2} p_0 \approx \frac{1}{4} p_{\text{lungs}}$.

About 1/3 of the myoglobin sites are used to transport oxygen to the tissues.

Transport will occur as long as the O_2 pressure in the tissue is less than that in the lungs.

Solution

First look at the lungs. Ignore the effect of the oxygen on the myoglobin to which it binds, so it's just like the problem of adsorption by surface sites.

Equilibrium is described by: $\mu_{\text{gas}} = \mu_{\text{bound}}$.

The fraction of occupied myoglobin sites is: $f = \frac{N_B}{M} = \frac{p_{\text{O}_2}}{p_{\text{O}_2} + p_0}$

We can't calculate p_0 , but we know empirically that $f \approx 2/3$ in the lungs. Also, since the atmosphere is 21% oxygen, we have $p_{\text{O}_2} = p_{\text{lungs}} \approx 0.2 \text{ atm}$.

Solving the above formula for p_0 , we find

$$f = \frac{p_{\text{O}_2}}{p_{\text{O}_2} + p_0} = \frac{1}{1 + p_0 / p_{\text{O}_2}} \Rightarrow 1 + p_0 / p_{\text{O}_2} = \frac{1}{f} \Rightarrow p_0 / p_{\text{O}_2} = \frac{1}{f} - 1$$
$$\Rightarrow p_0 = p_{\text{O}_2} \left(\frac{1}{f} - 1 \right) = 0.2 \left(\frac{3}{2} - 1 \right) = 0.1 \text{ atm}$$

What happens in the tissue?

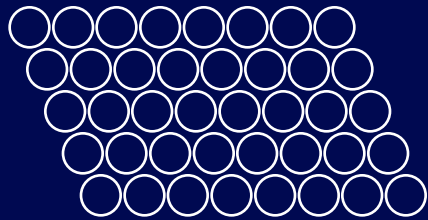
p_0 is the same, but here $p_{\text{O}_2, \text{tissue}}$ is lower, only $\sim 0.05 \text{ atm}$.

This drops f to $0.05 / (0.05 + 0.1) = 1/3$.

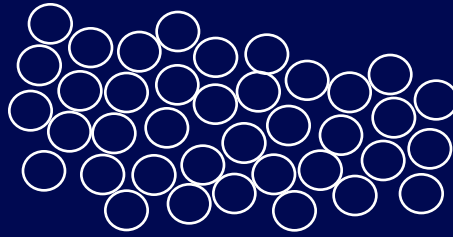
i.e., about 1/3 of the myoglobin sites are used to transport oxygen to the tissues.

Transport will occur as long as the O_2 pressure in the tissue is less than that in the lungs.

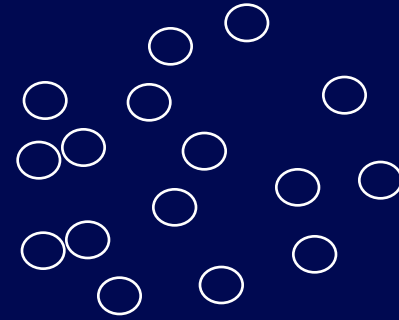
Solids, Liquids and Gases



Solid



Liquid



Gas

Solids have fixed relationships among the atoms (or molecules)

Liquids have looser relationships among atoms.

⇒ The liquid has more entropy, because there are more ways to arrange atoms in the liquid.

In liquids there are still some correlations between atoms, but in gases there are essentially none. In most situations the entropy of the gas is vastly larger than that of the liquid or solid.

Act 2

If gases always have more entropy than liquids, which have more entropy than solids, why isn't everything a gas (since the 2nd Law states that entropy should always increase)?

A) The 2nd Law only applies to static systems, not ones where a transition is occurring.

B) The 2nd Law only applies to 'isolated systems', and the substances here aren't isolated.

C) Wait long enough – eventually everything *will* be a gas!

Solution

If gases always have more entropy than liquids, which have more entropy than solids, why isn't everything a gas (since the 2nd Law states that entropy should always increase)?

A) The 2nd Law only applies to static systems, not ones where a transition is occurring.

B) The 2nd Law only applies to 'isolated systems', and the substances here aren't isolated.

C) Wait long enough – eventually everything *will* be a gas!

The energy transfer to cause the transition had to come from/go to somewhere, decreasing or increasing the entropy of THAT. The 2nd law applies to the total entropy of everything involved in the process.

I'm not sure if this is true.

For: the universe is expanding → more entropy as things spread out

Against: black holes (but even they evaporate...)

Phase Transitions and Entropy

If $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$, why are different phases stable at different temperatures?

The answer is that we must also consider the entropy of the environment.
That's what free energy and chemical potential do for us.

For example: At low enough temperatures a substance like water is a solid. Its entropy is lower than that of the liquid so it must give up enough energy* to its environment to make the total entropy increase when ice forms:

$$\text{Liquid H}_2\text{O} \rightarrow \text{Solid: } \Delta S_{\text{tot}} = \underbrace{\Delta S_L + \Delta S_S}_{< 0} + \underbrace{\Delta S_{\text{env}}}_{> 0} \geq 0$$

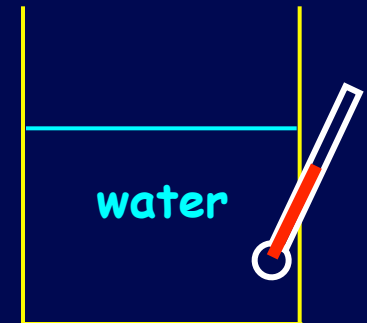
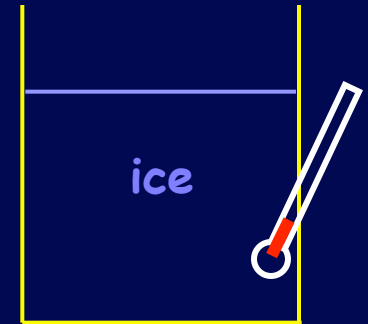
In order for this to work, enough heat must be given to the environment to make $\Delta S_{\text{tot}} \geq 0$.

OK. So, why is liquid H_2O favored at higher temperatures?

The relative sizes of the ΔS terms must be different.

Next time we'll look at the problem more quantitatively.

*The energy released is called the 'latent heat' – more on this next time.



Next time

- Phase diagrams
- Latent heats
- Phase-transition fun