Miscellaneous Notes

- The end is near – don't get behind.
- **All Excuses must be taken to 233 Loomis before noon, Thur, Apr. 25.**
- The PHYS 213 final exam times are
  * 8-10 AM, Monday, May 6

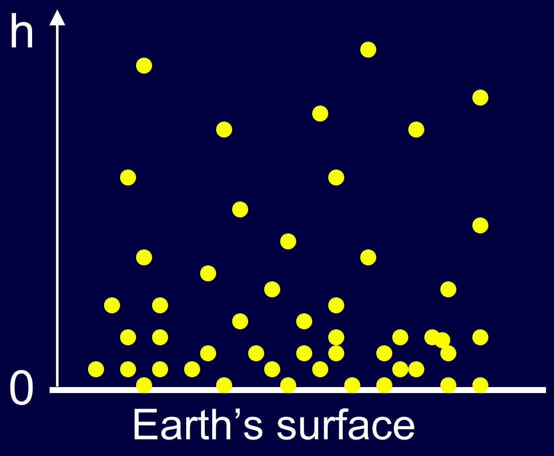
  * 1:30-3:30 PM, Wed, May 8

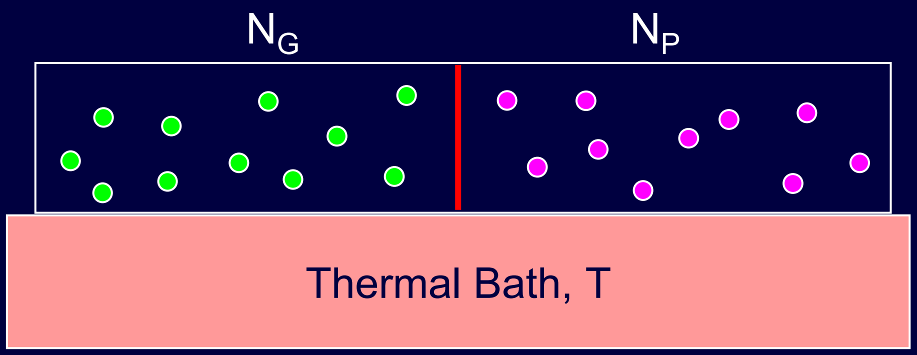
  The deadline for changing your final exam time is 10 pm, Tuesday, April 30

- Homework 6 is due <u>Tuesday</u>, Apr. 30 at 8 am. (NO late turn-in).
- Course Survey = 2 bonus points (accessible in SmartPhysics, but not until Apr. 24)

Lecture 18

Review & Examples



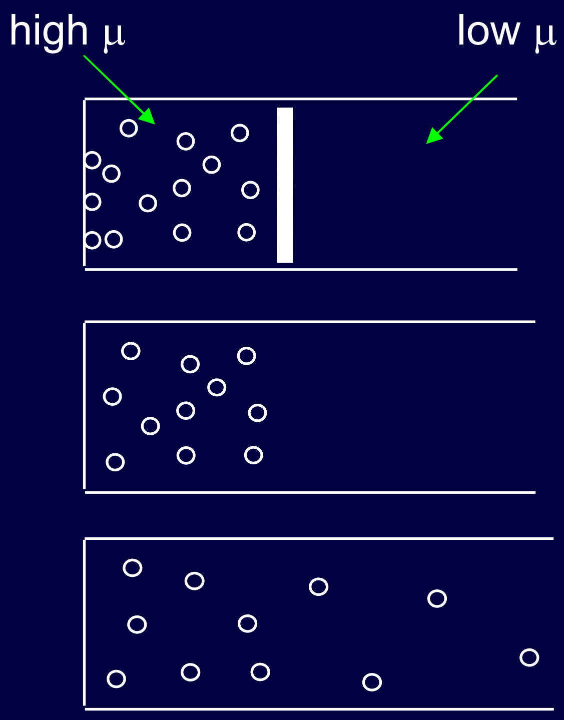


Physical Significance of μ

Last time we looked at the chemical potential for an ideal (monatomic) gas:

$$\boxed{\mu \equiv \left.\frac{\partial F}{\partial N}\right|_{V,T} = u + kT\ln\left(\frac{n}{n_Q}\right)}$$

Consider the case of no external potential (u is a constant):
$\mu = kT\ln(n) - \text{constant}$. Apply it to the free expansion problem:



Remove the piston:

Diffusion:
Particles move from high μ to low μ

Some time later:

In equilibrium, μ is the same everywhere.

Chemical Potential with Potential Energy

The potential energy per particle, PE, makes an additional contribution N·PE to the free energy: F = U - TS.

So, the chemical potential (μ = dF/dN) gains an additional contribution: d(N·PE)/dN = PE. It's the energy that one particle adds to the system.

$$\mu = kT\ln\frac{n}{n_T} + PE$$

n = N/V particle density

Examples:

Atom in gravity:

$$\mu = kT\ln\frac{n}{n_T} + mgh$$

Molecule with binding energy, Δ:

$$\mu = kT\ln\frac{n}{n_T} - \Delta$$

Simple example:

The Law of Atmospheres (1)

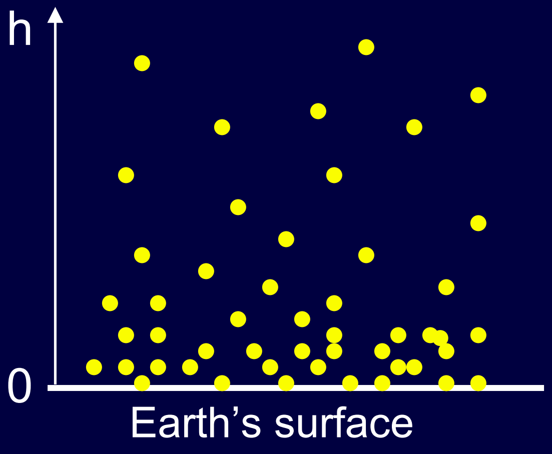
Question:

How do the gas density n and pressure p of the gas vary with height from the earth's (or any planet's) surface?

Compare region 2 at height h with region 1 at height 0. (equal volumes)

For every state in region 1 there's a corresponding state in region 2 with mgh more energy.

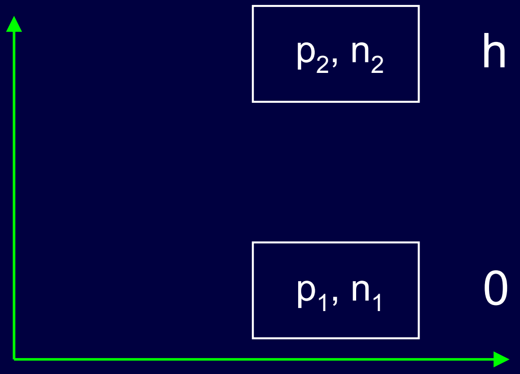
Assume that the temperature is in equilibrium ($T_1=T_2$).



Pressure:

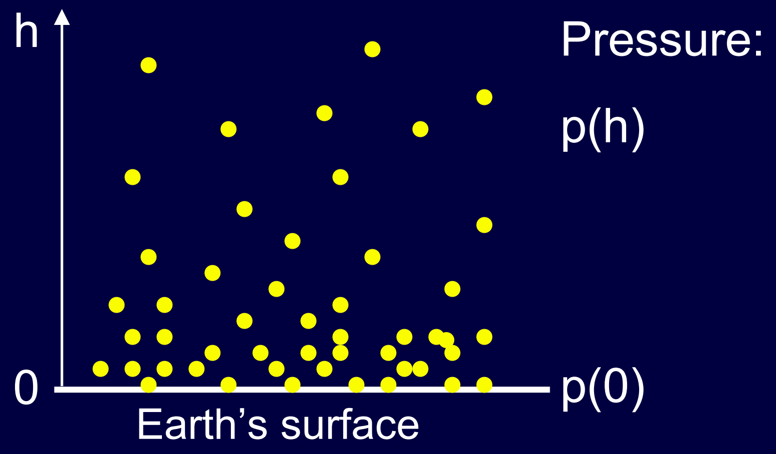
p(h)

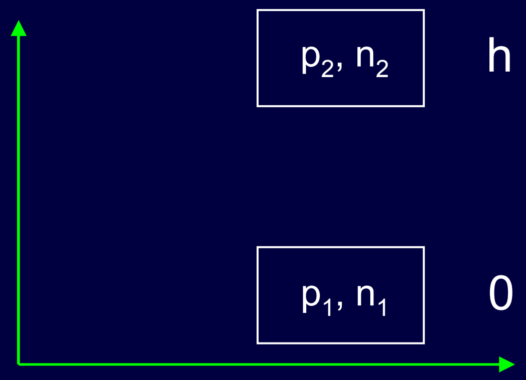
p(0)



Write the ideal gas law like this: $p = nkT$. ($n \equiv N / V$)

ACT 1





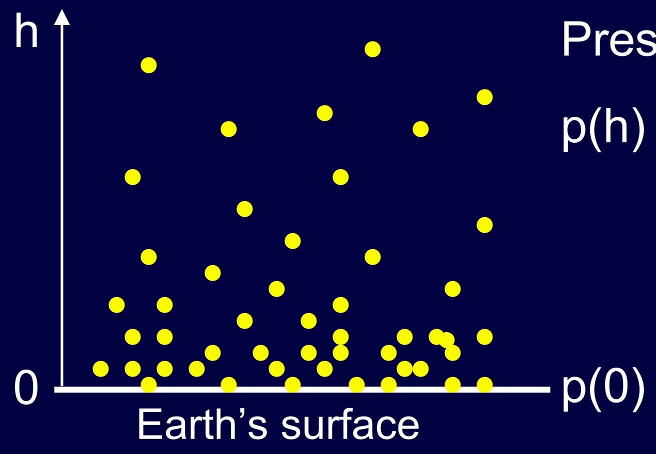
Assuming the system is in equilibrium, compare the chemical potentials at height 0 and height h:

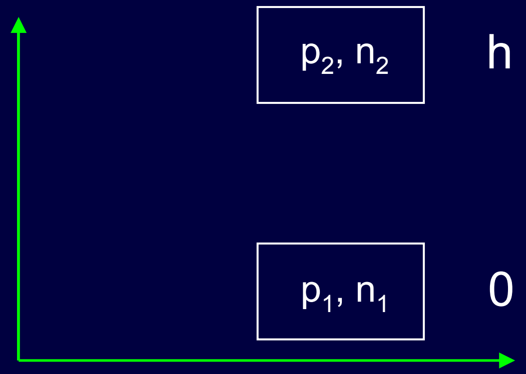
A) $\mu(0) < \mu(h)$

B) $\mu(0) = \mu(h)$

C) $\mu(0) > \mu(h)$

Solution





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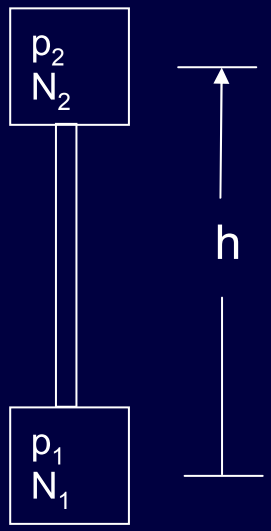
C) $\mu(0) > \mu(h)$

The potential energy part of the chemical potential is higher for the particles at h. The particle density part is higher for the particles at 0. But the total chemical potential *must* be the same at the two altitudes. Otherwise, the particles would move until the chemical potential *was* the same:

$$\mu(0) = \mu(h) \text{ in equilibrium}$$

The Law of Atmospheres (2)

The two regions can exchange particles (molecules), so imagine that they are connected by a narrow tube. The rest of the atmosphere is the thermal reservoir.



Equilibrium: $\mu_1 = \mu_2$

Chemical potential (ideal gas): $\mu_1 = kT\ln\frac{n_1}{n_Q}$

Solution: $\mu_2 = kT\ln\frac{n_2}{n_Q} + \text{mgh}$

$$kT\ln\frac{n_1}{n_Q} =$$

$$kT\ln\frac{n_2}{n_1} =$$

$$\frac{n_2}{n_1} =$$

Ideal gas law: p/n = kT **($T_1 = T_2$ in equilibrium)**

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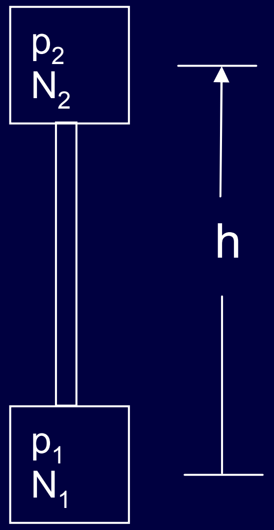

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Solution: $\mu_2 = kT \ln \frac{n_2}{n_Q} + \mathrm{mgh}$

$$kT \ln \frac{n_1}{n_Q} = kT \ln \frac{n_2}{n_Q} + \mathrm{mgh}$$

$$kT \ln \frac{n_2}{n_1} = -mgh$$

$$\frac{n_2}{n_1} = e^{-mgh/kT}$$

Ideal gas law: p/n = kT **($T_1 = T_2$ in equilibrium)**

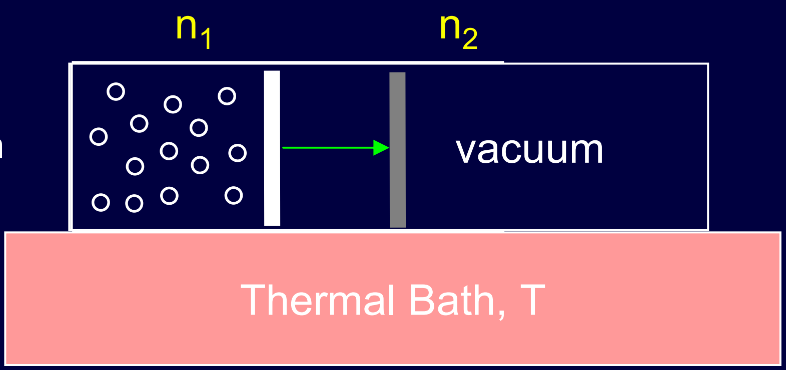
$$\Rightarrow \quad \frac{p_2}{p_1} = e^{-mgh/kT}$$

(a rigorous derivation of our earlier result.)

Work from Free Energy Due to Non-equilibrium μ

Mechanical Work (isothermal expansion of N particles at temp T)

Quasi-static expansion (an external force on the piston prevents it from being free expansion):



$$W_{by} = -\Delta F = -\Delta U + T\Delta S$$

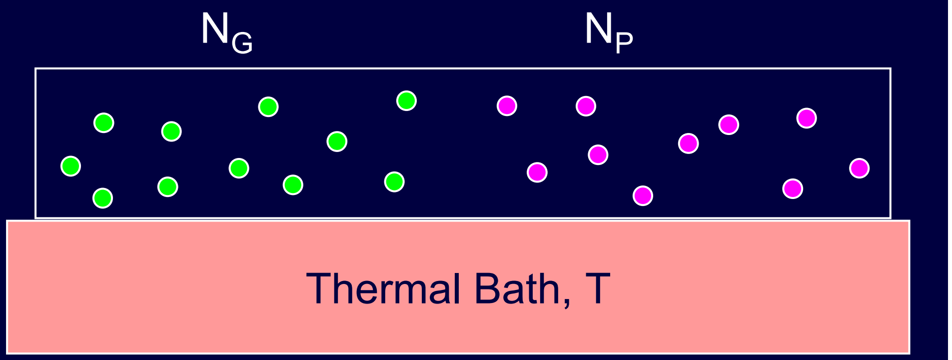
$$= NkT \ln(V_f/V_i)$$

Constant T $\Rightarrow$ $\Delta U = 0$ (ideal gas)

Look familiar? Same old physics, different language.

Can we use these concepts to do something new ???

ACT 2

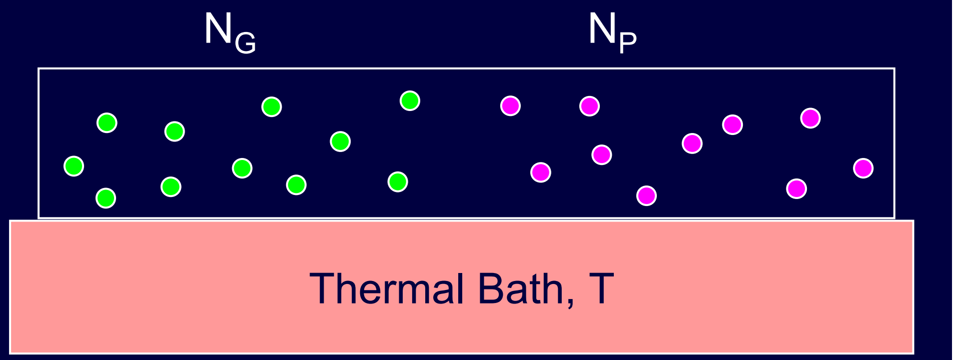


Consider this situation.
Two different ideal gases,
at equal pressures.
If one starts on the left,
and one on the right,
each will expand to fill the volume.

In his situation, how much work, if any, could be extracted?

A) 0 B) $(N_G - N_P)\,kT$ C) $(N_G+N_P)\,kT*\ln(2)$

Solution



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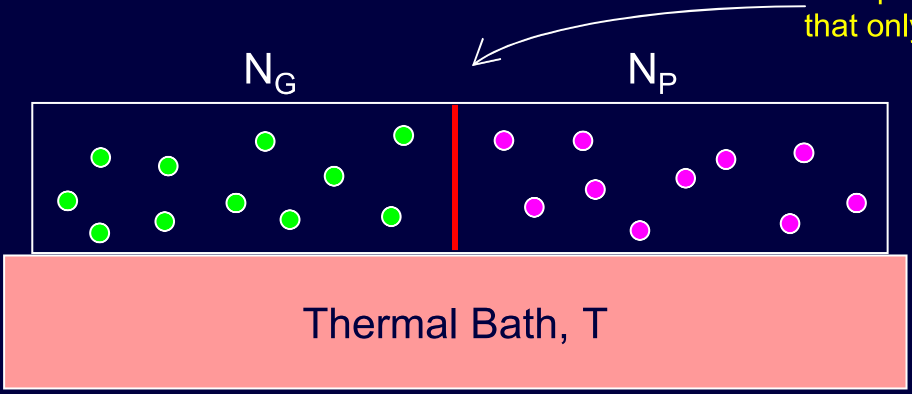
Each of the components individually loses free energy in the expansion (after the expansion, there's obviously no longer the possibility of expanding and doing work!); therefore, each component individually could do work up to $\Delta F = N\, kT \ln 2$.

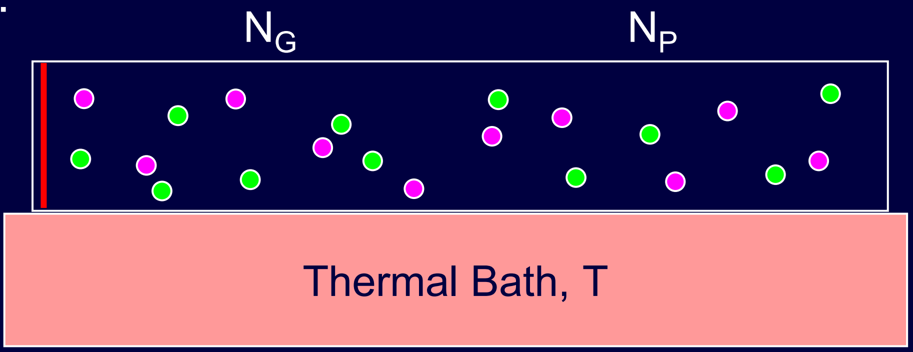
Can we actually get work out of this system?

How to Get the Workout



Semipermeable membrane
that only lets green molecules through.

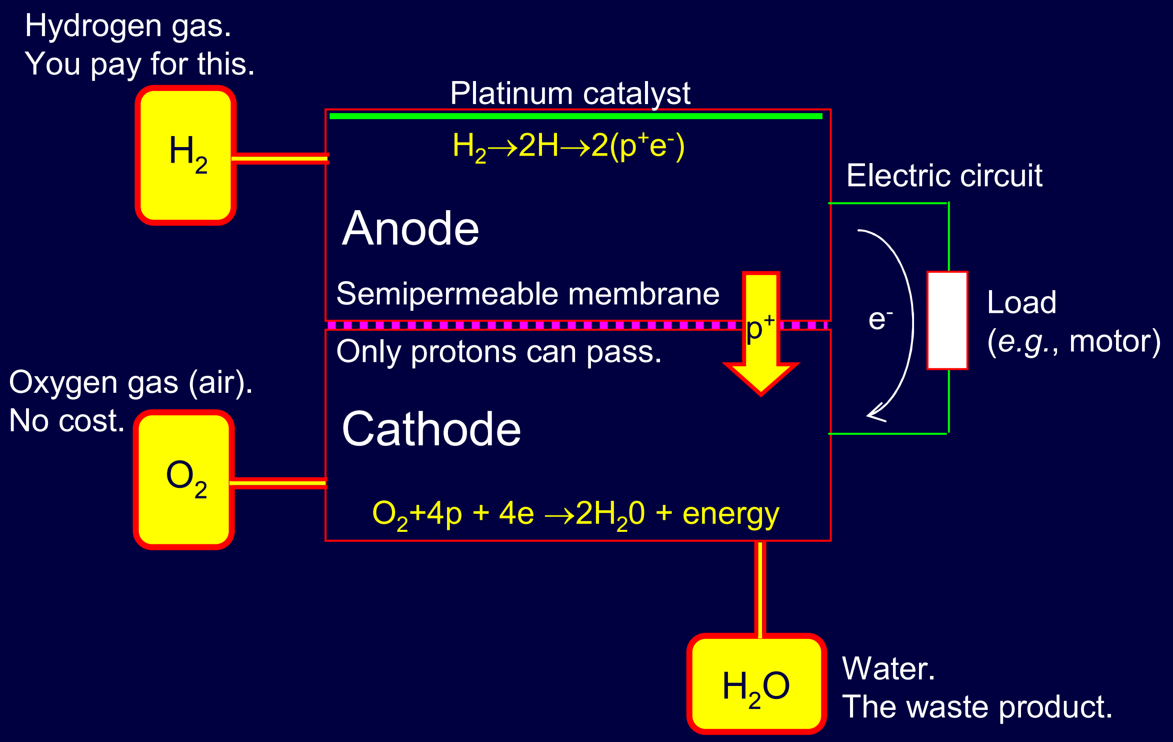
Equilibrium:



Both gases will have expanded to fill the entire volume. The purple molecules will have done work, $W = N_p kT\ln 2$, on the membrane (quasistatic expansion). The free energy of the green molecules is lost (free expansion).

Question: Can we get the green gas to do work as well?

Fuel Cells



Hydrogen gas.
You pay for this.

H_2

Platinum catalyst

$H_2 \rightarrow 2H \rightarrow 2(p^+e^-)$

Electric circuit

Anode

Semipermeable membrane

p^+

e^-

Load
(*e.g.*, motor)

Only protons can pass.

Oxygen gas (air).
No cost.

O_2

Cathode

$O_2 + 4p + 4e \rightarrow 2H_20 + \text{energy}$

H_2O

Water.
The waste product.

The fuel cell requires concentration gradients in two places:

- At the platinum catalyst. Keep the concentration of p^+ and e^- below equilibrium value, so the reaction will continue. Proton diffusion out of the anode (through the membrane) does this.
- Between the cathode and anode. Keep the proton (and electron) concentration low on the cathode side, so diffusion will continue. Water production does this.

Fuel Cells (2)

The semipermeable membrane forces the electrons to take a different path to the low concentration region. This path, through the load, is where we get useful work from the fuel cell.

Unlike typical heat engines, which first burn fuel to make heat, there is no conversion to heat. → no Carnot efficiency limit.

The platinum catalyst speeds the $H_2 \rightarrow 2(p^+e^-)$ reaction by increasing the H_2 concentration locally (at the surface). We'll see next week that

$$\frac{n_{H_2}}{n_p^2 n_e^2} = K$$

Fuel cells are used in specialty applications. However:

> "Top executives from General Motors Corp. and Toyota Motor Corp. Tuesday expressed doubts about the viability of hydrogen fuel cells for mass-market production in the near term and suggested their companies are now betting that electric cars will prove to be a better way to reduce fuel consumption and cut tailpipe emissions on a large scale." (WSJ, 3/5/2008)

ACT/Discussion: Converting Fuel to Work

- The work output comes from the excess free energy (above the equilibrium value) of the starting chemicals (the fuel).
- In an atmosphere containing O_2, H_2 is fuel.
- There's lot's of H_2 in the H_2O in the oceans.
- Do we therefore have plenty of fuel?

A) yes B) no C) maybe

Solution

- The work output comes from the excess free energy (above the equilibrium value) of the starting chemicals (the fuel).
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- Do we therefore have plenty of fuel?

A) yes [✓ B) no] C) maybe

Not from this source. The hydrogen in the water is in thermal and chemical equilibrium, so its free energy is minimum.

If we have another energy source (*e.g.*, solar), we can use it to dissociate the H_2O, and then carry the H_2 around. This might be useful, but the H_2 is not the fuel; it’s just the energy transport medium.

Build Your Intuition

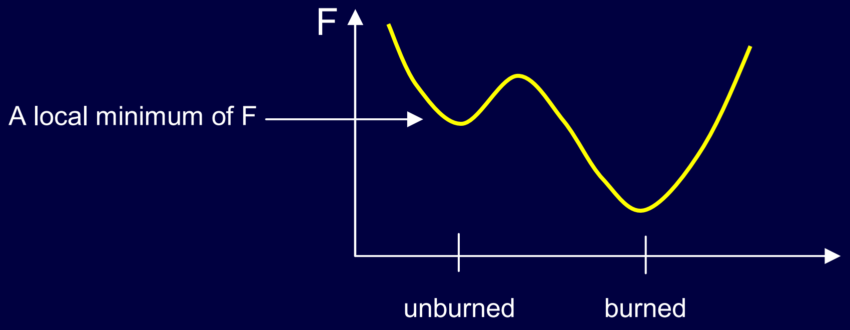
A process will happen spontaneously if the free energy would be decreased.

This is just another way of saying that, left on their own, systems will tend to thermal equilibrium, *i.e.*, minimum free energy.

If you have to do work on a system (the opposite of a spontaneous process), you are increasing the free energy of the system.

Why do matches burn (after you strike them)?
The burned state has less free energy than the unburned state.

Why must you strike the match?
There is an energy barrier - it needs help getting started.



ACT 3:
Chemical Potential of Diatomic Gas

How does including the rotational energy and entropy of H_2 change its μ, compared to what you'd have if it were monatomic?

In other words, what is the effect on F per molecule?

A) No change B) Decreases μ C) Increases μ D) Not enough info

Solution

How does including the rotational energy and entropy of H_2 change its μ, compared to what you'd have if it were monatomic?

In other words, what is the effect on F per molecule?

A) No change B) Decreases μ C) Increases μ D) Not enough info

Molecular rotation increases U. → Increases F.
It also increases S (more microstates). → Decreases F.

Which effect is larger?

The addition of rotation modes must decrease F !!! (proof on next slide)
If F were not lowered when the molecules rotated, they would not rotate!

What does this do to equilibrium?
μ_{H2} is now less than $2\mu_H$, so the reaction will proceed in the direction of increasing n_{H2}, until equality is restored.

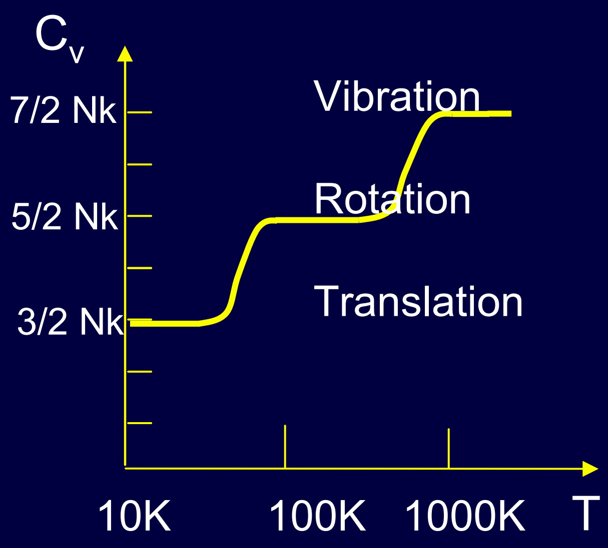
$$\mu = kT\ln\frac{n}{n_T} - \Delta$$

Contribution of Internal Modes to μ

Proof that internal modes lower F:

For ideal gases, the internal contributions to F are independent of the other contributions.

F_{int}/N is their contribution to $\mu = dF/dN$



$$F_{int} = U_{int} - TS_{int}$$

We can calculate F_{int} by remembering that the internal modes contribute to $C_V(T)$:

$$U_{int} = \int_0^T C_{V(int)}(\tau)d\tau \qquad S_{int} = \int_0^T \frac{C_{V(int)}(\tau)}{\tau}d\tau$$

$$F_{int} = U_{int} - TS_{int} = \int_0^T \left(1 - \frac{T}{\tau}\right) C_{V(int)}(\tau)d\tau < 0$$

This is always true, because C_V is always positive.
So the thermal excitation of the internal modes of a molecule always lowers its μ, and thus increases its equilibrium concentration.