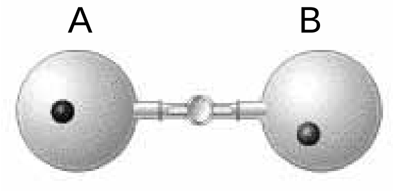
February 6, 2002

- Exam #1
  - Wednesday, 2/13, 7 pm
  - *Conflict?* Email me this week
- **Day/time for Exam Review Session?**
- **Exam #1 Info Page now online!**
- **Old Exam #1 Questions now online!**

A Little Experiment

Consider the following:



- Two bulbs of equal volume
- Equal number of molecules in each bulb
- *What is the probability of finding ALL of the molecules in Bulb A?*

# molecules	relative probability
1	1/2
2	$1/(2)^2$ (= 1/4)
5	$1/(2)^5$ (= 1/32)
10	$1/(2)^{10}$ (=1/1024)

For 1 mol gas, changing orientations 100 times/sec:

- Event would occur *once* every 10^{14} **years**

Entropy of Physical States

$$S_{solid} < S_{liquid} < S_{gas}$$

increasing number of possible orientations

So, for a phase change:

Solid → Liquid (spontaneous at $T > T_f$)

Liquid → Gas (spontaneous at $T > T_b$)

$\boxed{\Delta S > 0}$

But, also:

Why spontaneous?

Gas → Liquid (spontaneous at $T < T_b$)

Liquid → Solid (spontaneous at $T < T_f$)

$\boxed{\Delta S < 0}$

How is Entropy Quantified?

On the *microscopic* level:

$$\boxed{S = k_B \ln W}$$

Boltzmann's constant (= R/N_o)

# of microstates

- Entropy *increases* with an increasing number of microstates (increased "disorder")
- **Units:** $k_b = 1.38 \times 10^{-23}$ J/K (so units of S are: J/K)

Macroscopic Entropy

- For a *reversible process* at *constant pressure*:

$$\Delta S_{sys} = \frac{q_{p,\,rev}}{T} = \frac{\Delta H}{T_{sys}}$$

•And don't forget:

$$\Delta S_{surr} = -\frac{\Delta H}{T_{surr}}$$

Now, let's revisit the freezing process for water . . .

Freezing Water: *Revisited*

$$H_2O\ (l) \rightarrow H_2O\ (s) \qquad \Delta H = -\ 6.0\ kJ/mol$$

- Freezing is an *exo*thermic process
- Energy flows from the system to the surroundings:
  - Entropy of the surroundings *increases*
  - Entropy of the system **decreases**
- **Suppose:** $T_{surr} < T_{sys}$ such that T_{surr} is less than FP
  - ΔS_{surr} is ***more positive*** than ΔS_{sys} is negative
  - $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ = ***positive*** (freezing is spontaneous)

Quantifying *Spontaneity*

Making some substitutions, we find:

$$\Delta S_{univ} = \Delta S_{sys} - \Delta H / T$$

Re-arranging gives:

$$T\Delta S_{univ} = T\Delta S_{sys} - \Delta H$$

Reversing signs:

$$-T\Delta S_{univ} = \Delta H - T\Delta S_{sys}$$

ΔG (Gibb's Free Energy)

The Gibbs-Hemholtz Equation

So, at constant temperature and pressure:

$$\boxed{\mathbf{DG = DH - TDS}}$$

Has units of *Joules* (energy): ***Free* Energy**

- Tells us how much energy is available to do work

All values are for the *system*

What happens at T=0?

We "break even"; *all energy is available to do work.*