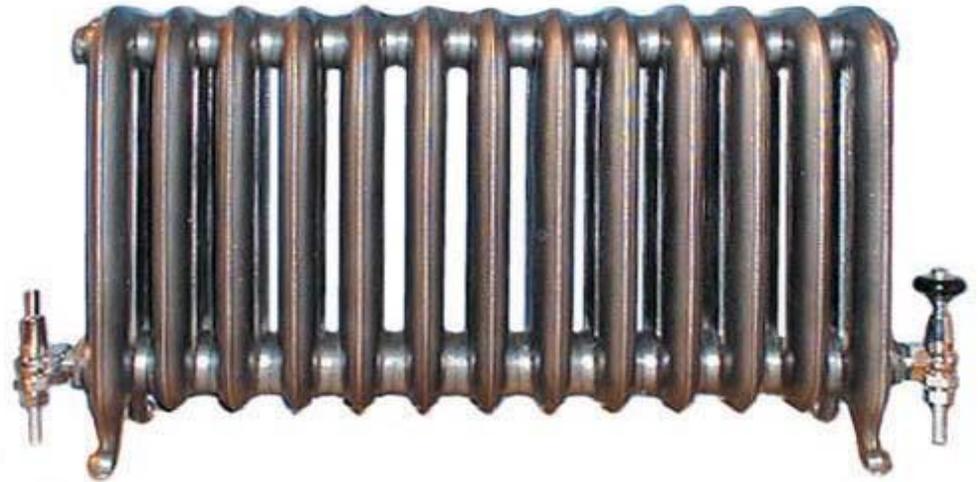




Chemical Thermodynamics



Recall that, at constant pressure, the enthalpy change equals the heat transferred between the system and its surroundings.

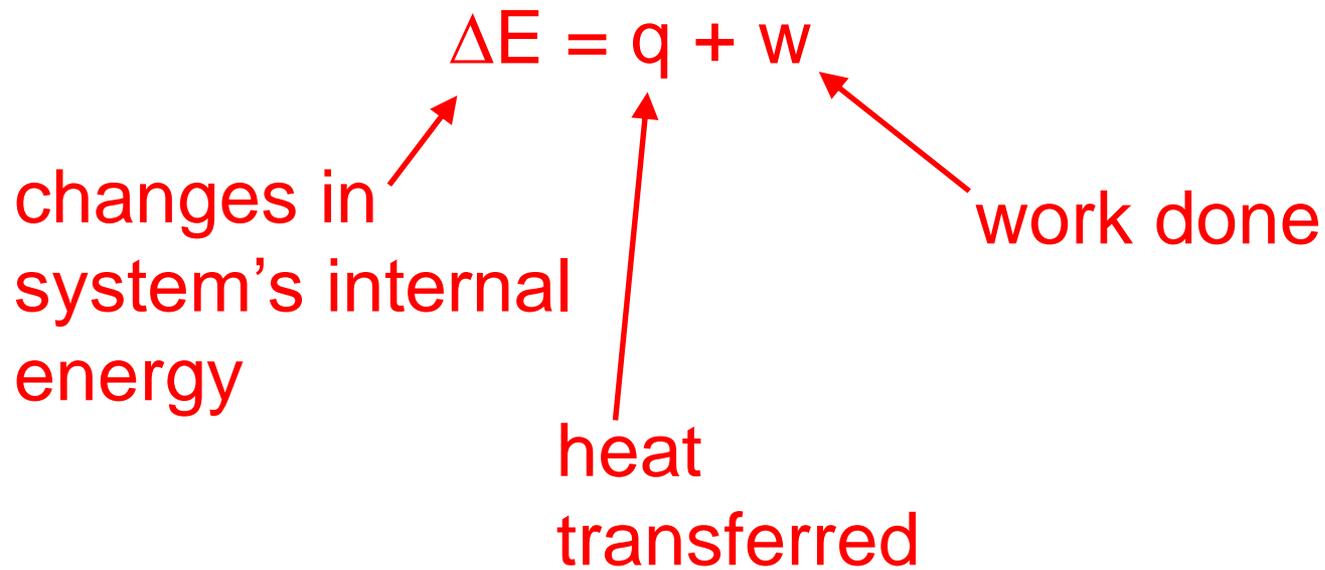
$$\Delta H = H_{\text{final}} - H_{\text{initial}} = q_p$$



Thermodynamics involves enthalpy changes AND changes in order/disorder.

spontaneous processes: ones that occur without outside intervention

The First Law of Thermodynamics: **Energy is conserved.**



If q is —, system released heat.

If q is +, system absorbed heat.

If w is —, system did work.

If w is +, system had work done on it.

Sign conventions are from system's point of view.

reversible process: “undo exactly what you did and you’ve got what you started with”

-- both system and surroundings go back to original states

-- e.g., changes of state

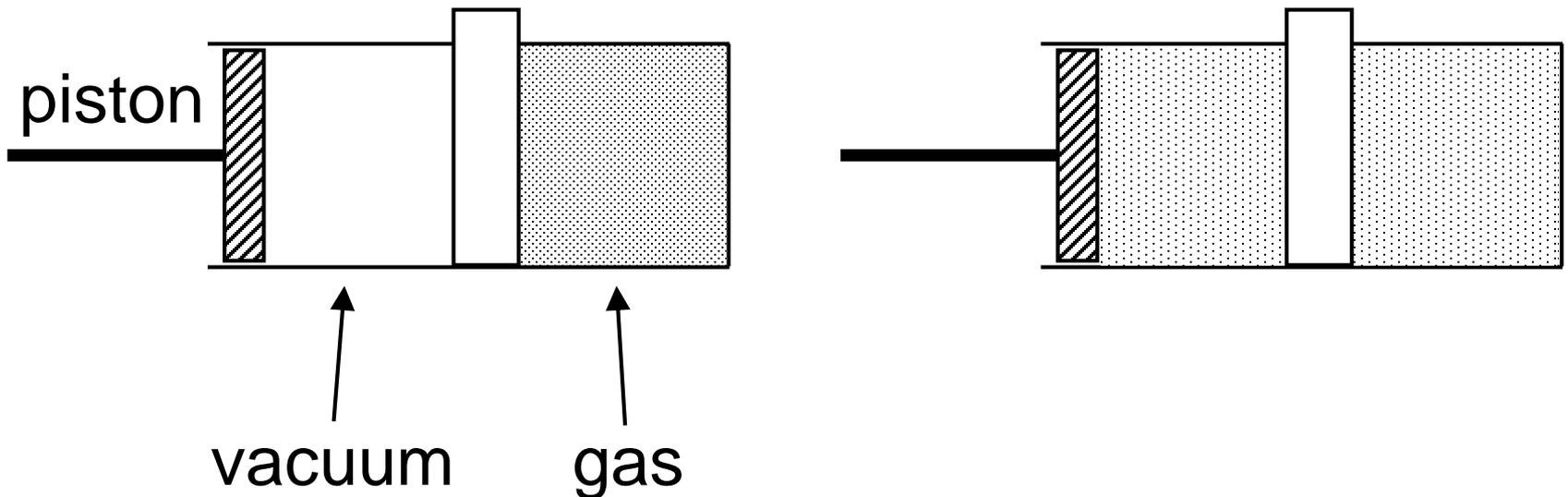
ice @ 0°C $\xrightleftharpoons[\text{take away } X \text{ J}]{\text{add } X \text{ J}}$ water @ 0°C



irreversible process: getting back what you started with
requires more than just an “undo”

-- we can restore the original system, but the
surroundings will have changed

-- e.g., a gas expanding into an evacuated space



Points of note:

1. Whenever a chemical system is in equilibrium, we can go reversibly between reactants and products.
2. In any spontaneous process, the path between reactants and products is irreversible.
3. Thermodynamics refers to the direction of a reaction, not its speed.
4. In general, exothermic processes are more likely to be spontaneous.

Processes in which the system's randomness increases tend to occur spontaneously.

$$\Delta S = S_f - S_i$$

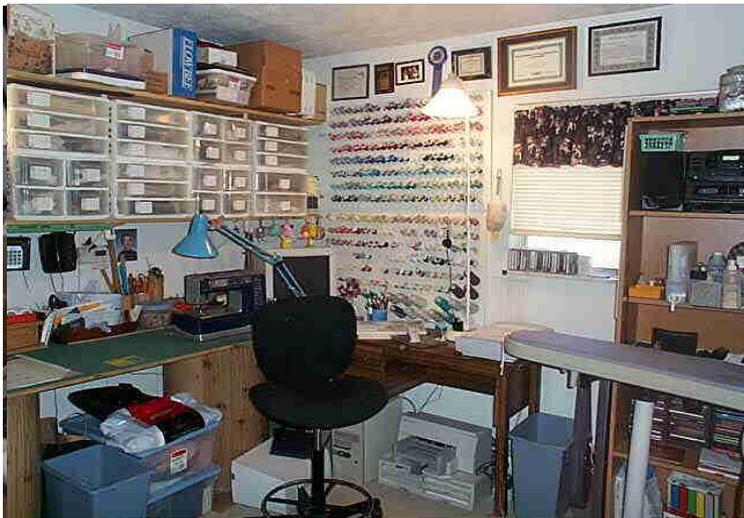
entropy, S

+ $\Delta S \rightarrow$ P are MORE random than R

- $\Delta S \rightarrow$ P are LESS random than R

large entropy = large # of microstates = very disordered

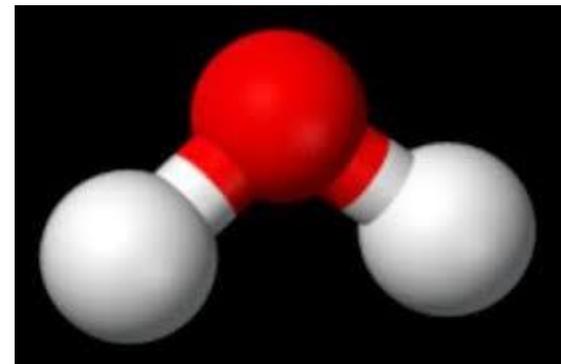
small entropy = small # of microstates = less disordered



Entropy at the Particle Level

There are three types of motion, each having kinetic energy (KE).

- translational, vibrational, rotational
- **The more KE we have, the more entropy we have.** (i.e., the more microstates are possible)



In general... As $T \uparrow/\downarrow$, $S \uparrow/\downarrow$.

and... $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$

Process	freezing	melting	condensing	boiling
Sign of ΔS	—	+	—	+

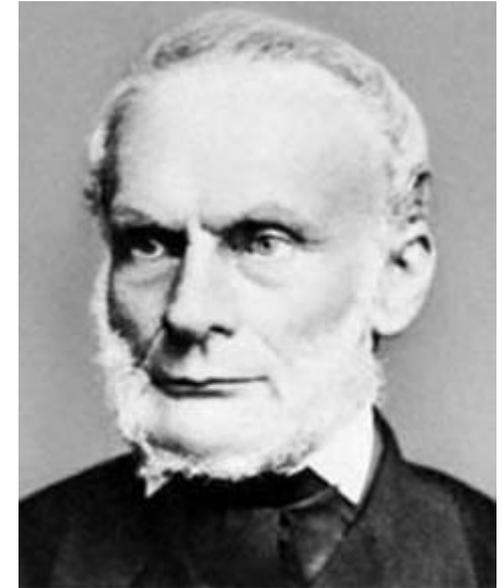
The Second Law of Thermodynamics:

The entropy of an isolated system that is NOT in equilibrium will increase over time.



Sadi Carnot
(1796–1832)

The entropy of the universe increases in any spontaneous process.



Rudolf Clausius
(1822–1888)

Entropy is NOT conserved; it is constantly increasing.

For isolated systems... rev. $\rightarrow \Delta S_{\text{sys}} = 0$

irrev. (i.e., spont.) $\rightarrow \Delta S_{\text{sys}} > 0$

For a system in which heat is transferred at constant temperature...

$$\Delta S = \frac{q}{T}$$

-- T in K

-- common unit for entropy $\rightarrow \frac{\text{J}}{\text{K}}$

i.e., heat (energy)
temperature

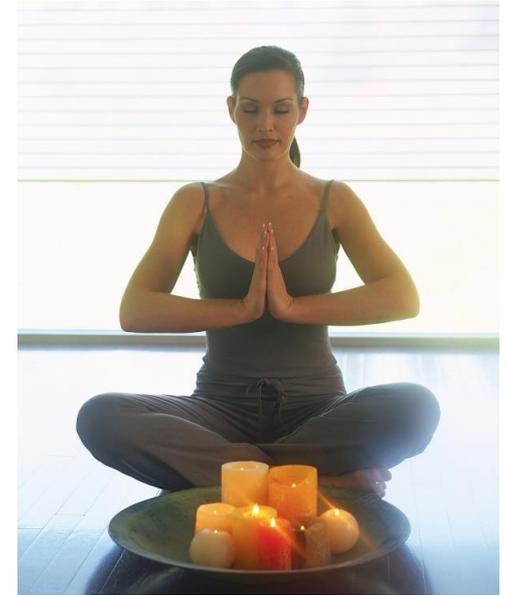
Find the change in entropy when 87.3 g of water vapor condense, given that water's heat of vaporization is 5.99 kJ/mol.

$$\begin{aligned}\Delta S &= \frac{q}{T} = \frac{m \Delta H_{\text{vap}}}{T} = \frac{87.3 \text{ g} \left(\frac{1 \text{ mol}}{18 \text{ g}} \right) \left(-5.99 \frac{\text{kJ}}{\text{mol}} \right)}{373.15 \text{ K}} \\ &= \boxed{-0.0779 \frac{\text{kJ}}{\text{K}}} = \boxed{-77.9 \frac{\text{J}}{\text{K}}}\end{aligned}$$

Third Law of Thermodynamics:

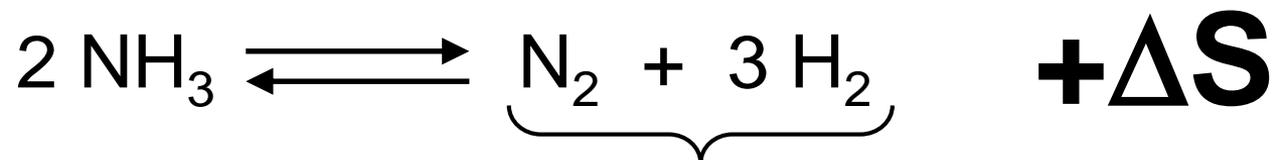
The entropy of a pure, crystalline substance at absolute zero is...ZERO.

- that would be a state of perfect order (impossible)



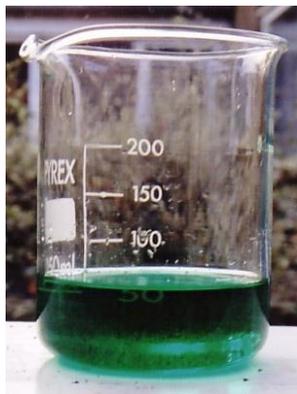
Entropy increases when:

1. the number of gas particles increases



fewer restrictions on motion of atoms;
more degrees of freedom;
more possible microstates

2. liquids or solutions
are formed from solids



3. gases are formed
from liquids or solids



Which has the greater entropy?

1 mol O₂(g) @ 300 K or 1 mol O₂(g) @ 500 K
(same volume)

1 mol KCl(s) @ 300 K or 1 mol HCl(g) @ 300 K

2 mol HCl(g) @ 300 K or 4 mol HCl(g) @ 300 K
(same volume)

1 mol HCl(g) @ 300 K or 1 mol Ar(g) @ 300 K
(same volume)

2 mol HCl(g) @ 300 K (in a 10-L vessel) or 2 mol HCl(g) @ 300 K (in a 5-L vessel)

Calculating Entropy Changes

standard molar entropies, S° : molar entropy values of substances in their standard states

(i.e., pure substances at ~1 atm)

←
actually, at 1 bar = 10^5 Pa = 0.987 atm

S° values typically...

- are NOT zero
- \uparrow ^w/increasing molar mass
- \uparrow ^w/increasing # of atoms in formula

In a chemical reaction...

$$\Delta S^\circ = \sum n S^\circ_P - \sum m S^\circ_R$$

(n and m are the coeff. for each substance)

Calculate the standard entropy change for...



177

223

353

tabulated values of
 S° in J/mol-K

$$\Delta S^\circ = \sum n S^\circ_{\text{P}} - \sum m S^\circ_{\text{R}}$$

$$\Delta S^\circ = 4(353) - [177 + 10(223)]$$

$$= -995 \text{ J/K}$$

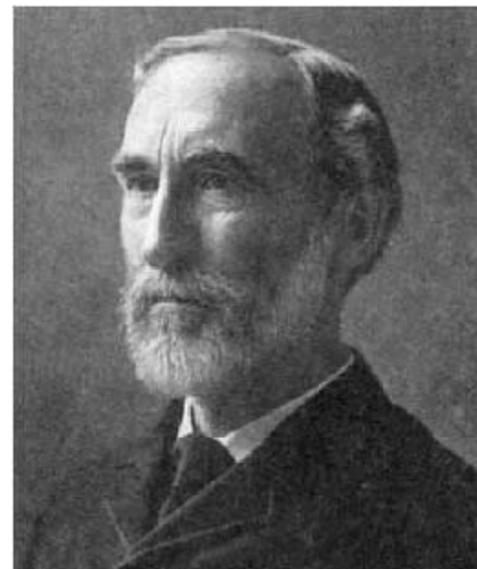


DANGER!

White phosphorus (or “WP”) is used in bombs, artillery shells, and mortar shells that burst into burning flakes of phosphorus upon impact.

Gibbs Free Energy

Enthalpy changes (ΔH) and entropy changes (ΔS) both have a “say” in whether or not a rxn is spontaneous. Spontaneity is determined using the equation for Gibbs free energy...



Josiah Willard Gibbs
1839–1903

$$\Delta G^{(o)} = \Delta H^{(o)} - T\Delta S^{(o)}$$

(^o) = std. conditions are optional

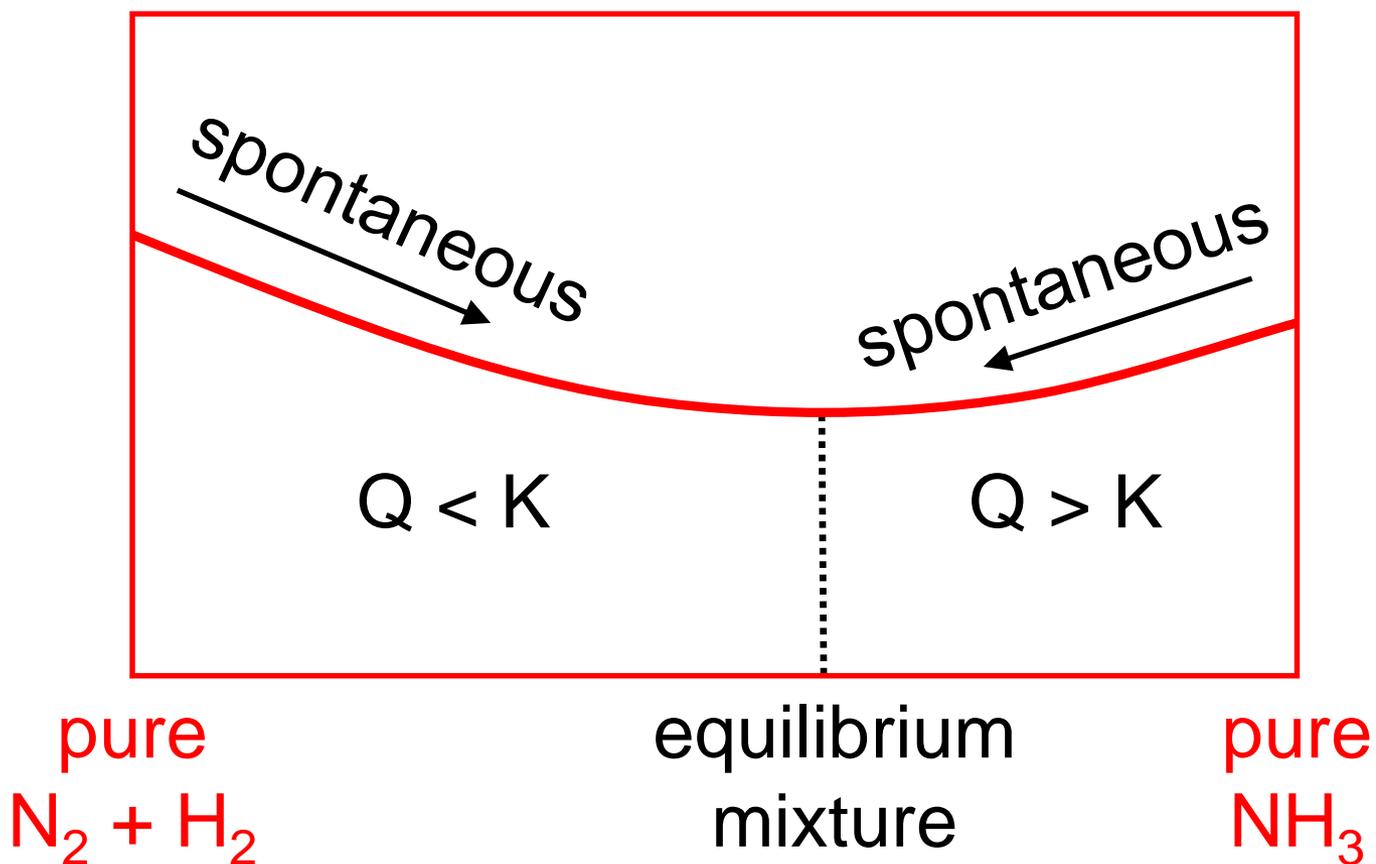
If $\Delta G < 0$... rxn. is spontaneous (i.e., as written)

If $\Delta G > 0$... rxn. is nonspontaneous (i.e., spont. \leftarrow)

If $\Delta G = 0$... rxn. is AT equilibrium

(THIS INCLUDES PHASE CHANGES AT NBP OR NFP)

For the Haber process...



standard free energies of formation, ΔG_f°

- are tabulated for pure solids, pure liquids, gases at ~1 atm pressure, and 1 M solutions
- For elements in their standard states... $\Delta G_f^\circ = 0$
- For a reaction, the standard free-energy change is found by...

$$\Delta G^\circ = \sum n G_f^\circ \text{P} - \sum m G_f^\circ \text{R}$$



ΔG says WHICH WAY a reaction will proceed, but it says NOTHING about the reaction rate.

Free Energy and Temperature

From $\Delta G = \Delta H - T\Delta S$, we see that ΔG varies with temperature.

-- When T changes, so does ΔG .

-- ΔH and ΔS change little with temperature.



EX. (a) Calculate ΔH° , ΔG° , and ΔS° for...



ΔH_f° (kJ/mol)	90.3	0	33.2
ΔG_f° (kJ/mol)	86.7	0	51.8
S° (J/mol-K)	210.7	205	240

$$\Delta H^\circ = 2(33.2) - [2(90.3)] \quad \Delta H^\circ = -114.2 \text{ kJ}$$

$$\Delta G^\circ = 2(51.8) - [2(86.7)] \quad \Delta G^\circ = -69.8 \text{ kJ}$$

$$\Delta S^\circ = 2(240.0) - [205.0 + 2(210.7)] \quad \Delta S^\circ = -146.4 \text{ J/K}$$

(b) Estimate ΔG at 400 K.

(Remember: ΔH and ΔS
vary very, VERY
little w/temp.)

$$\Delta G = \Delta H - T\Delta S$$

$$= -114,200 \text{ J} - [400 \text{ K}(-146.4 \text{ J/K})]$$

$$= -55,600 \text{ J}$$

$$= -55.6 \text{ kJ}$$

Estimate the normal boiling point of ethanol.



Strategy: Realize that $\Delta G = 0$.

Find ΔS and ΔH .

Solve for T in $\Delta G = \Delta H - T\Delta S$.

	L	G
S° (J/mol-K)	160.7	282.7
ΔH_f° (kJ/mol)	-277.7	-235.1

$$\Delta S \cong \Delta S^\circ = 122 \text{ J/K} \quad \Delta H \cong \Delta H^\circ = 42.6 \text{ kJ}$$

$\Delta G = \Delta H - T\Delta S \dots$ $T = \frac{\Delta H}{\Delta S} = \frac{42,600 \text{ J}}{122 \text{ J/K}} = 349 \text{ K (76}^\circ\text{C)}$

$$\Delta H = 42,600 \text{ J}; \Delta S = 122 \text{ J/K}$$

We estimated 76°C; the actual NBP of ethanol is 78.4°C.

From $\Delta G = \Delta H - T\Delta S$, we see that spontaneity (i.e., ΔG) depends on T.



Assume we start at 78.4°C, where $\Delta G = 0$...

As T increases, ΔG becomes

-- spontaneous, liquid to gas

As T decreases, ΔG becomes

-- spontaneous, gas to liquid

Free Energy and the Equilibrium Constant

ΔG° is the standard free-energy change
(i.e., for a reaction at standard conditions).

Under **any other** conditions...

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$R = 8.314 \text{ J/mol-K}$$

$$Q = \text{rxn. quotient}$$



**Comparatively few reactions
take place under standard
conditions.**

Calculate ΔG at 298 K, given the following:



(non-standard pressures) 1.0 atm 3.0 atm 0.50 atm

ΔG_f° (kJ/mol)	0	0	-17
-----------------------------	---	---	-----

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = 2(-17) = -34 \text{ kJ} = -34,000 \text{ J}$$

$$Q = \frac{(0.50)^2}{(1.0)(3.0)^3} = 0.00926$$

$$\Delta G = -34,000 + 8.314 (298) (\ln 0.00926)$$

$$\Delta G = -45.6 \text{ kJ}$$

At equilibrium, $\Delta G = 0$ and $Q = K$, so..

$$\Delta G^{(o)} = -RT \ln K$$

and

$$K = e^{-\Delta G^{(o)}/RT}$$

For gas-phase rxns, the K is K_p ; for rxns. in soln, it is K_c .

Calculate ΔG° and K at 298 K for...

Assume all gases are at 1.00 atm of pressure.

$$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g})$$

ΔG_f° (kJ/mol)	0	3.14	-53.22
-----------------------------	---	------	--------

$$\Delta G^\circ = 2(-53.22) - 3.14 = -109.58 \text{ kJ}$$

$$K = e^{-\Delta G^\circ/RT} = e^{+109,580/(8.314)(298)} = 1.6 \times 10^{19}$$

Rxn. is

***What if we are relating/trying-to-find ΔG and/or K ,
but NOT at standard conditions?***

-- To approx. K , given ΔG and nonstandard T :

$$\text{Use } K = e^{-\Delta G/RT}$$

-- To approx. ΔG , given K and nonstandard T :

$$\text{Use } \Delta G = -RT \ln K$$

-- To approx. K , given rxn eq and nonstandard T :

1. Use tabulated values to calc. ΔH° and ΔS° , which are “good” for all temps.
2. Use $\Delta G = \Delta H - T\Delta S$ and answers above to approx. ΔG at desired temp.
3. Use $K = e^{-\Delta G/RT}$ to approx. K at desired temp.