4/10/19

Chapter 18: Free Energy + Thermodynamics

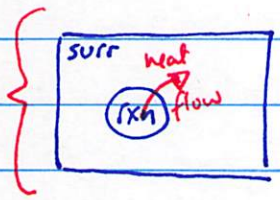
Ch6 : Thermochemistry : q_{rxn} ← heat

$\Delta H = q_{rxn}$ (const, p) ← enthalpy

if $\Delta H < 0$, $q_{rxn} < 0$, heat is lost (−) by rxn to surr

exothermic rxn (−ve)

UNIVERSE



<u>1st law of thermo</u>

→ Energy is conserved

→ E_{UNIV} = constant

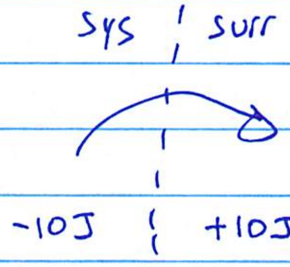
→ $\Delta E_{UNIV} = 0$

$$\Delta E_{sys} + \Delta E_{surr} = 0$$

(rxn)

$\Rightarrow \Delta E_{sys} = -\Delta E_{surr}$

1st law



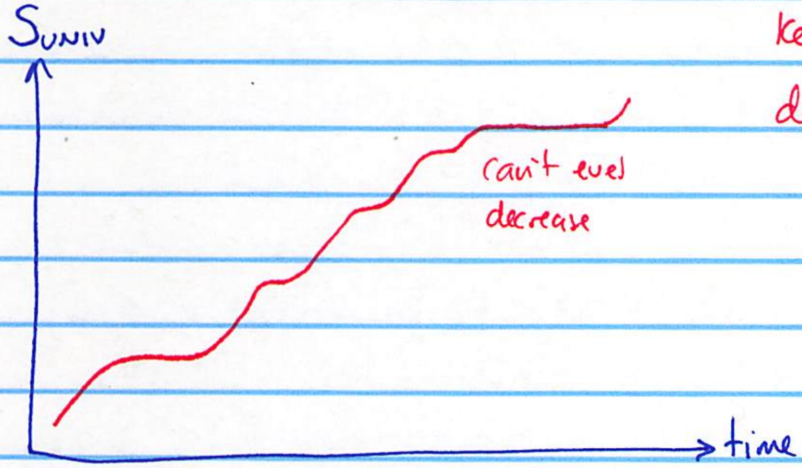
<u>Spontaneous</u>	<u>Non-Spontaneous</u>
will/can occur w/out input of E	will not occur w/out input of E
ex: ice melts on a hot day	ex: water freezing on a hot day
	– but if we place water in a freezer, water → ice.

Entropy + 2nd law of thermodynamics

↳ S ~ related to disorder/messiness ... but this is just an analogy
(symbol)

- state function
(changes in S are independent of path)

2nd law: $\Delta S_{UNIV} \geq 0$ (Universe's entropy must keep increasing ... never decreasing)

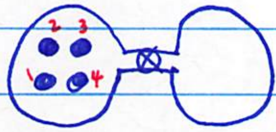


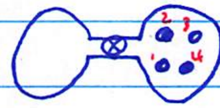
Boltzmann: $S = k \cdot \ln W$ ← # of microstates = # ways of arranging particles in a system w/ same E

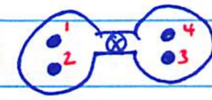
↑ Boltzmann's constant $= 1.38 \times 10^{-23}$ J/K

$k = \frac{R}{N_A}$ — R: gas constant, N_A: Avogadro's #

consider: ideal gas, 2 chambers, 4 atoms (1, 2, 3, 4) macrostates

(A) 

(B) 

(C) 

microstates

	left	right	l	r	l	r
	1,2,3,4			1,2,3,4	12	34
					13	24
					14	23
	W=1			W=1	23	14
					24	13
					34	12

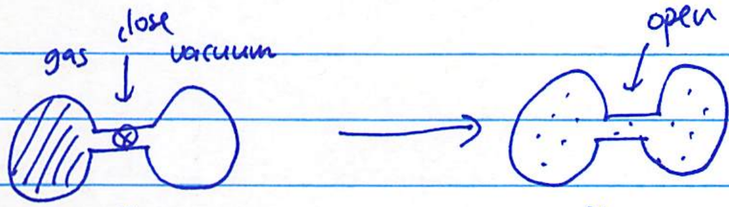
W=6 (C)

$S = K \cdot \ln W$

A and B: lowest entropy

C: highest entropy

2nd law: $\Delta S_{univ} \geq 0$ $\quad S\uparrow$

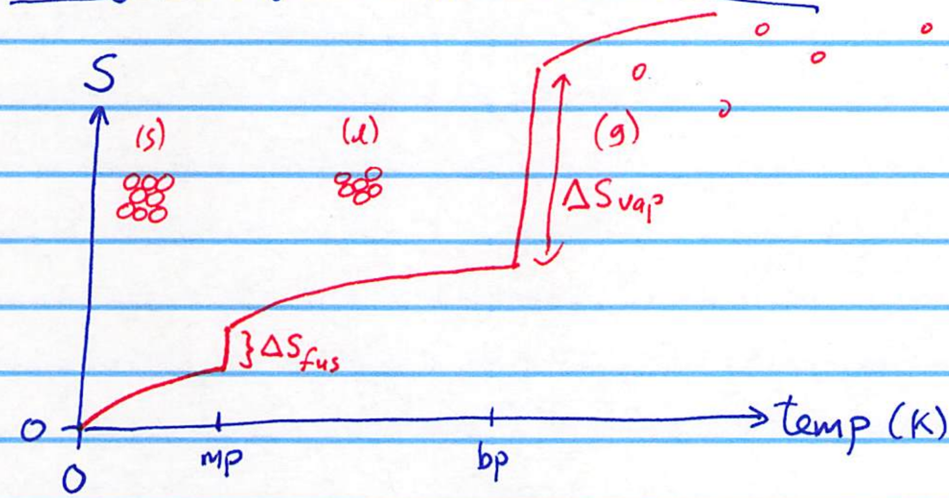


before
lower S

after
larger S

$\Delta S = S_{final} - S_{initial} = +ve \qquad (\Delta S > 0)$

Entropy changes during state/phase changes



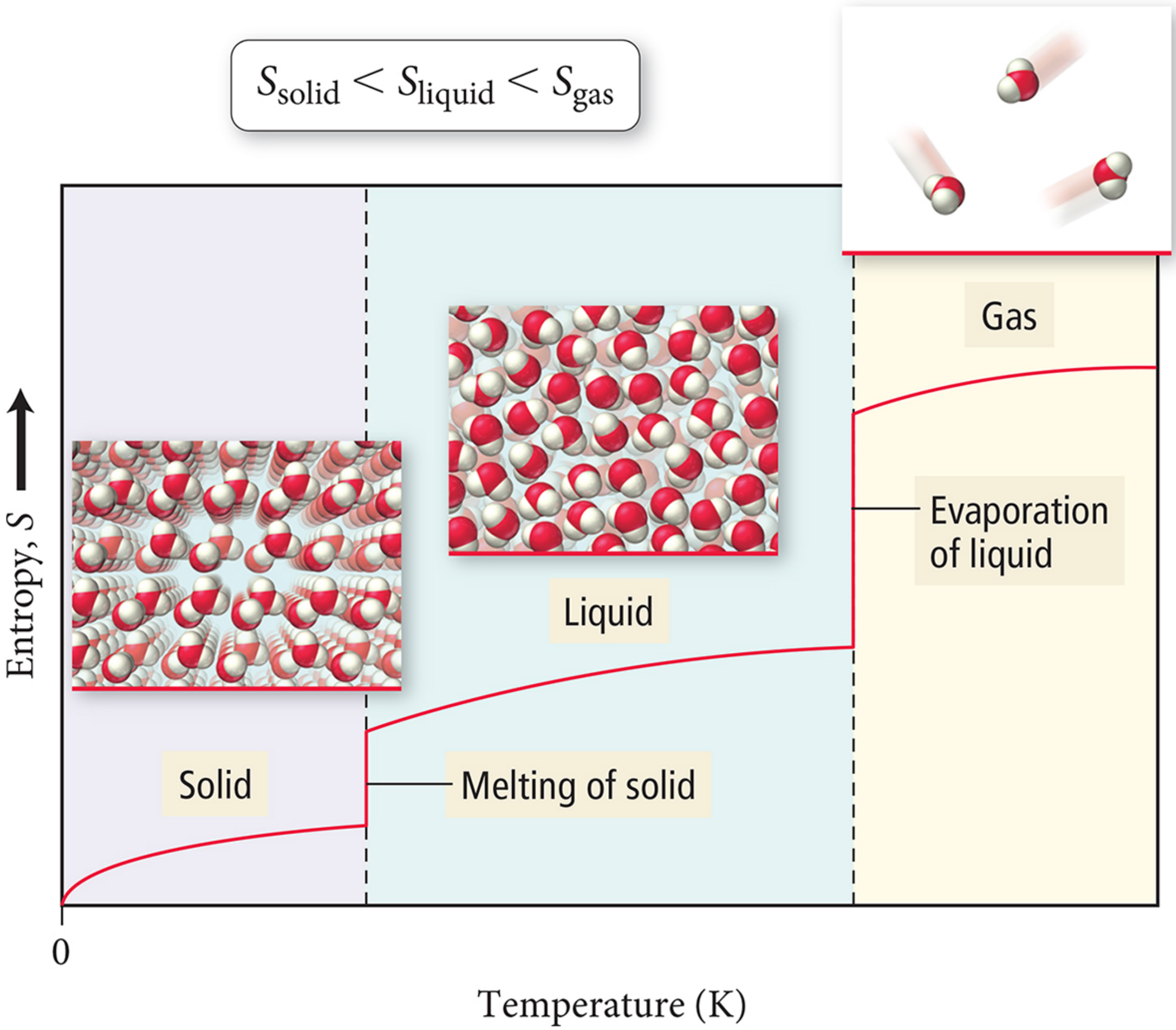
Know: s → l, l → g, s → g } $\Delta S > 0$

can guess: R → P } $\Delta S > 0$

fewer gas molecules → more gas molecules

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$; $\Delta S > 0$

0-gas → 1-gas (increase)


$S_{solid} < S_{liquid} < S_{gas}$
Gas
Evaporation of liquid
Liquid
Solid
Melting of solid
Entropy, S
0
Temperature (K)