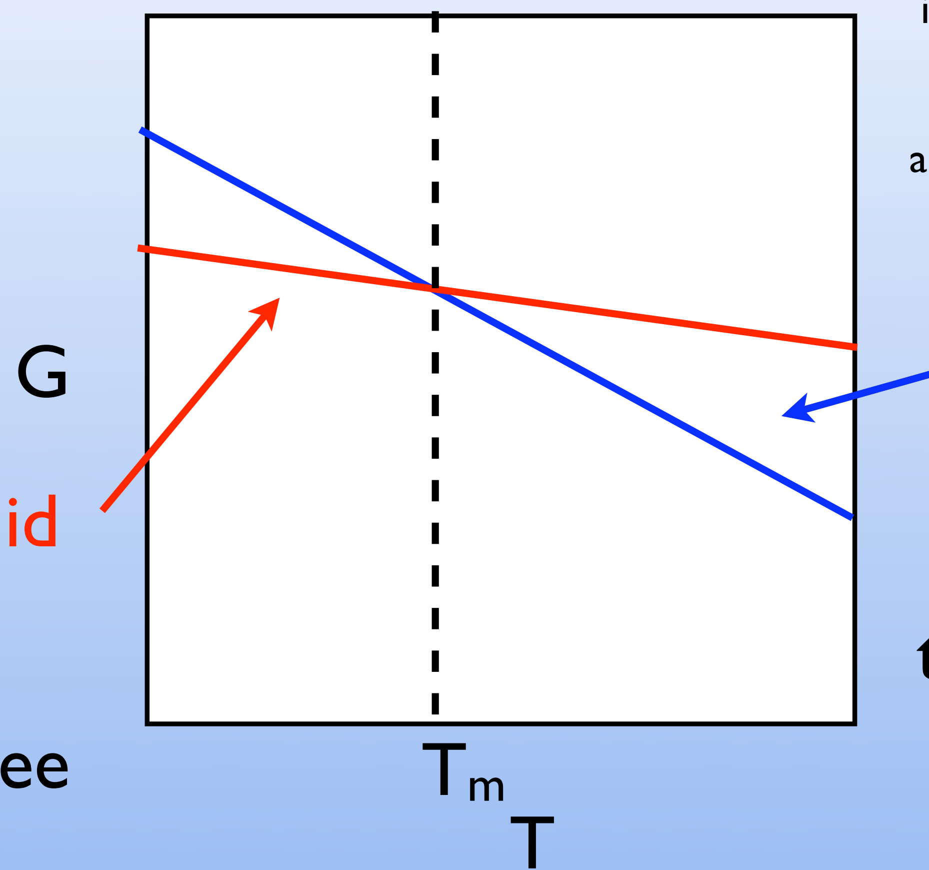
Just to be clear about Free Energy

$G = H - TS$

straight line assumes
that H and S are
independent of temperature
Slope is given by S
Liquid has a larger entropy
and therefore a steeper slope



$T < T_m$
Solid has
the lower free
energy

$T > T_m$
Liquid has
the lower free
energy

Super Cooled or Super Heated

Kinetically trapped in non-equilibrium state

"Super-cooled" trapped in liquid state
due to slow crystal formation

"Super-heated" trapped in liquid state
due to slow bubble formation

Demo

Last Phase change

What is a key difference between evaporation and boiling?

A. liquids only boil at 1 atm total pressure

B. liquids only evaporate at room temperature

C. bubble form in liquids when boiling

D. nothing

Solutions

Solutions are homogeneous mixtures
of multiple compounds

Solution	
	Major component = Solvent (language typically used for liquids)
salt water	
air	Minor component = Solute
steel	

Let's look at the following "reaction"

water + salt ------> "salt water"

Which has the higher entropy?

A. The water + the solid salt

B. The solution ←

C. They are exactly the same

Let's look at the following "reaction"

water + salt ------> "salt water"

Which has the lower free energy?

A. The water + the solid salt

B. The solution ←

C. They are exactly the same

Let's look at the following "reaction"

water + salt ------> "salt water"

Which has the higher enthalpy?

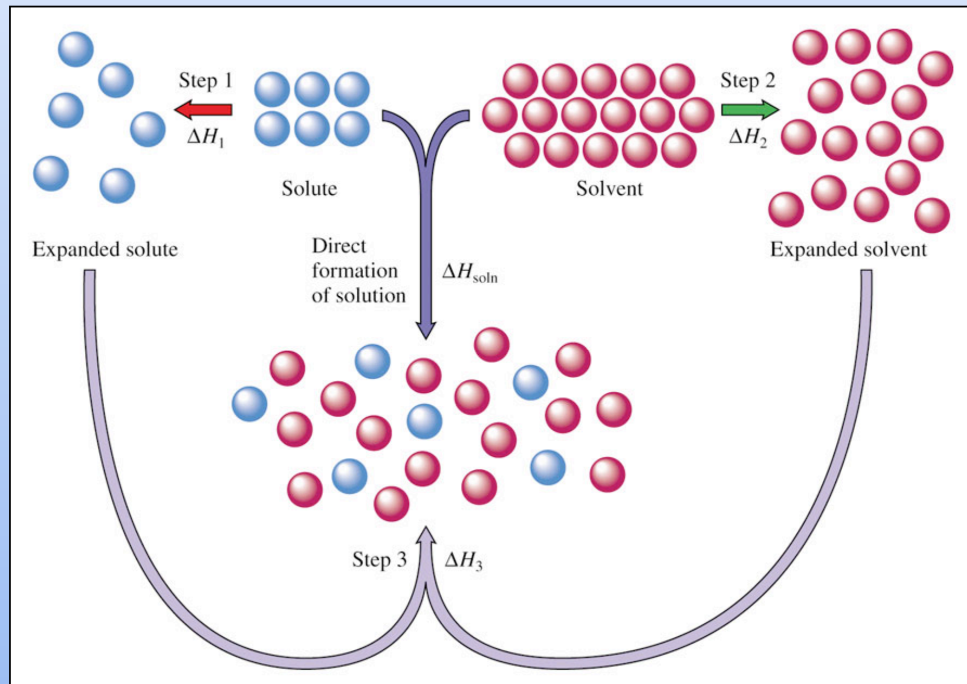
A. The water + the solid salt

B. The solution

C. They are essentially the same ←

What has to happen?

Lose solvent-solvent interactions (IMF)
Lose solute-solute interactions (IMF)
Gain solute-solvent interactions



Enthalpy of Solvation $\Delta H_{solvation}$ hard to predict

$\Delta H_{solvation} = 0$

Ideal solution

Solute-solvent interactions are identical to solute-solute and solvent-solvent

$\Delta H_{solvation} > 0$

Typical

Solute-solvent interactions are weaker than solute-solute and solvent-solvent

$\Delta H_{solvation} < 0$

Unusual but possible

Solute-solvent interactions are stronger than solute-solute and solvent-solvent

Entropy of Solvation $\Delta S_{solvation}$ easy to predict

Solutions have a higher entropy than the unmixed compounds

Therefore

$$\Delta S_{solvation} > 0$$

TABLE 17.2 Values of ΔS°_{soln} for Several Salts Dissolving in Water

Process	ΔS° ($J\ K^{-1}\ mol^{-1}$)
$KCl(s) \rightarrow K^{+}(aq) + Cl^{-}(aq)$	75
$LiF(s) \rightarrow Li^{+}(aq) + F^{-}(aq)$	−36
$CaS(s) \rightarrow Ca^{2+}(aq) + S^{2-}(aq)$	−138

Gibb's Free Energy of Solvation $\Delta G_{solvation}$

If $\Delta G_{solvation} < 0$ solution strongly favored

If $\Delta G_{solvation} > 0$ undissolved state is strongly favored

$$\Delta G_{solvation} = \Delta H_{solvation} - T\,\Delta S_{solvation}$$

Best case $\Delta H_{solvation} < 0$

Generally the best you can hope for is $\Delta H_{solvation} = 0$ ideal

What makes an ideal solution?

Same IMF for solute-solvent and
solute-solute and solvent-solvent

"like dissolves like"

Polar compounds dissolve polar compounds (ionic)

Nonpolar compound dissolve nonpolar compounds

Which is most likely to dissolve best in water?

A. methanol CH_3OH ←

B. butanol C_4H_9OH

C. octanol $C_8H_{17}OH$

D. didodecanol $C_{12}H_{25}OH$

Which is most likely to dissolve best in hexane (C_6H_{14})?

A. methanol CH_3OH

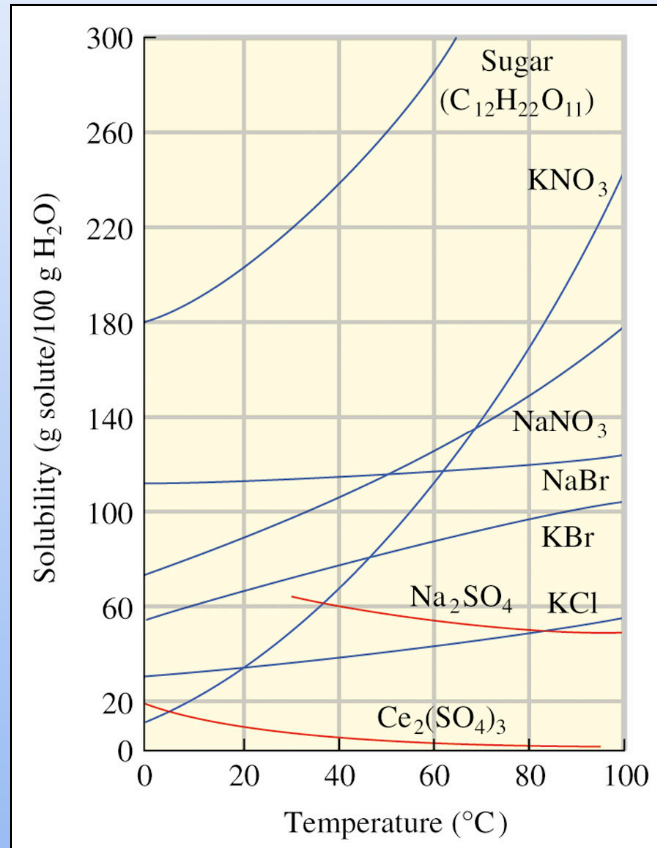
B. butanol C_4H_9OH

C. octanol $C_8H_{17}OH$

D. didodecanol $C_{12}H_{25}OH$ ←

Temperature Dependence

Generally at T goes up solubility increases



Gas Dissolved in a Liquid

Henry's Law

TABLE 17.3 The Values of Henry's Law Constants for Several Gases Dissolved in Water at 298 K

Gas	k_H (atm)
CH_4	4.13×10^2
CO_2	1.64×10^3
O_2	4.34×10^4
CO	5.71×10^4
H_2	7.03×10^4
N_2	8.57×10^4

$$P_{solute} = K_{solvent} X_{solute}$$

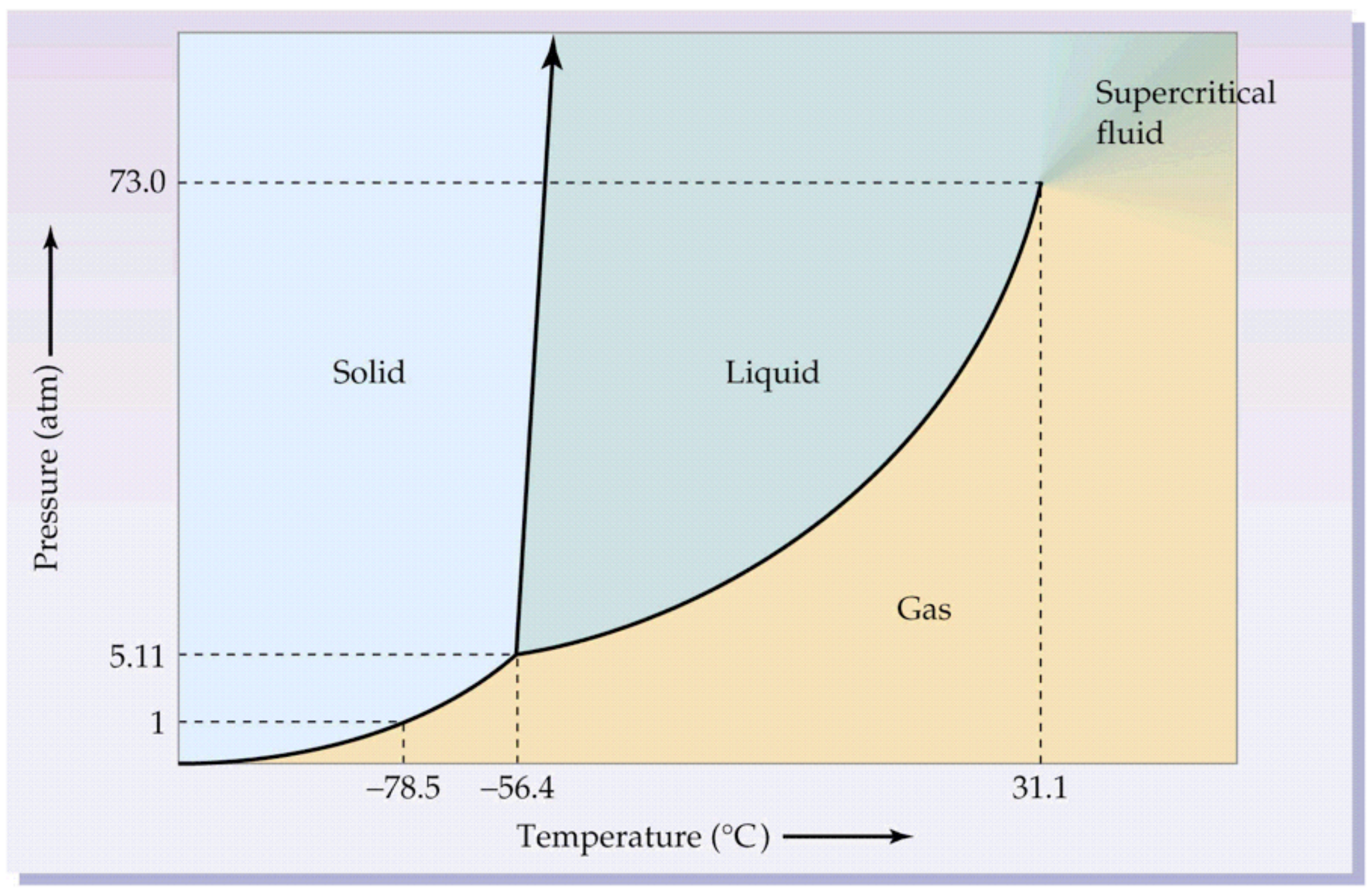
mole fraction (of X_{solute})

In General

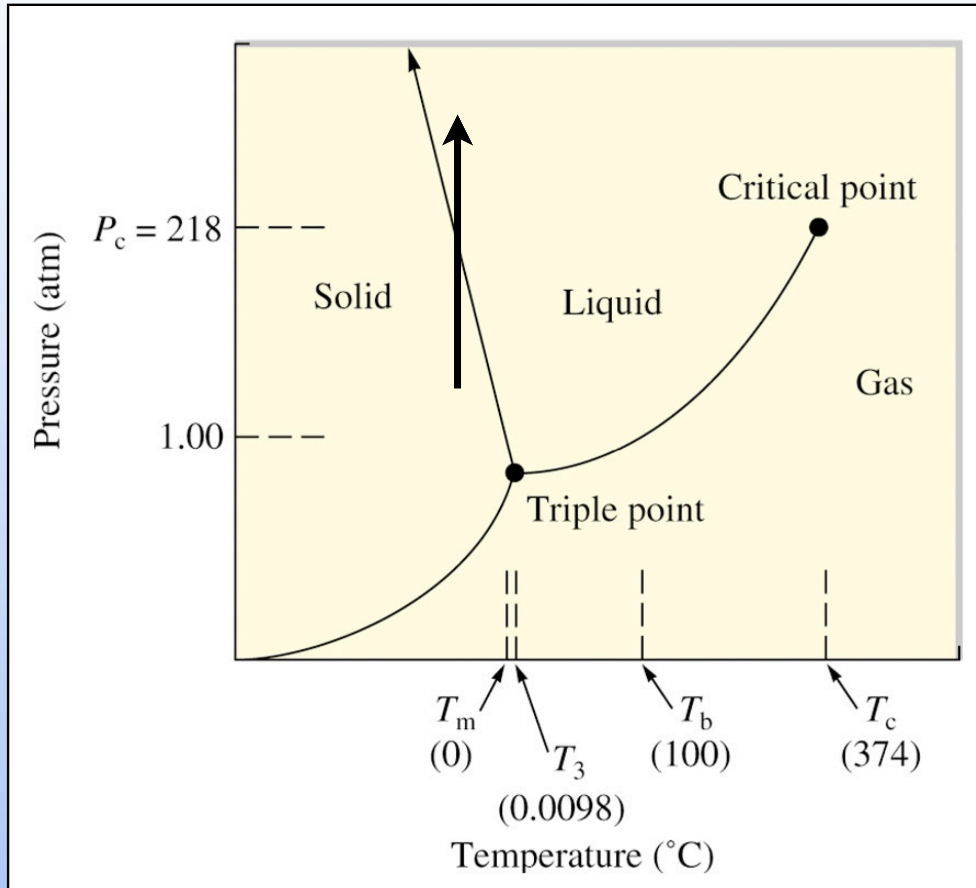
Henry's Law constants increase with increasing Temperature

Less gas is dissolved at higher temperatures

Phase Diagram of CO_2

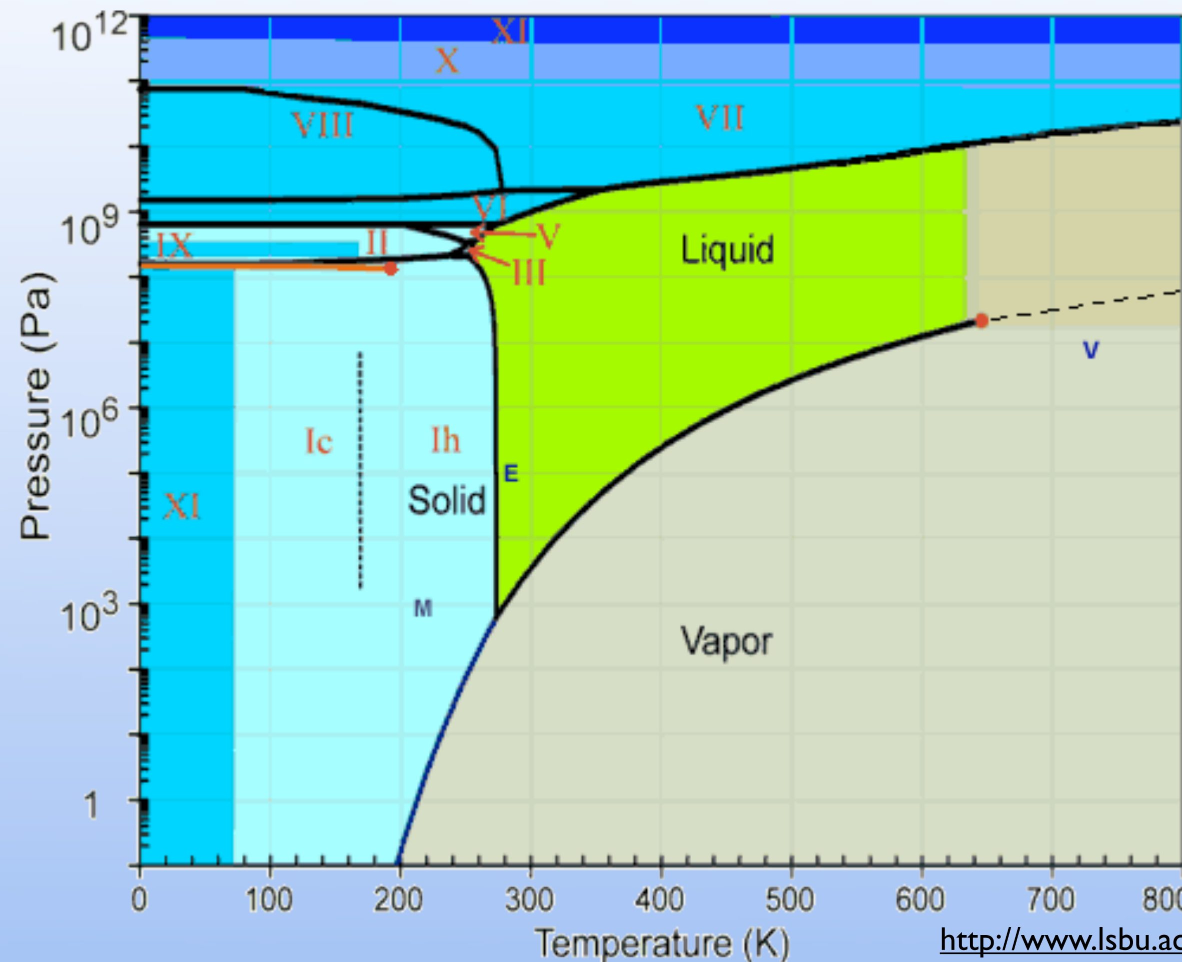


Phase Diagram of Water



At a constant temperature, increasing the pressure will cause ice to melt (it moves to the higher density phase which for water is a liquid)

Phase Diagram of Water



http://www.lsbu.ac.uk/water/images/phase.gif

Many different solid phases. At very high pressure the liquid will solidify

Other Substances