Nanotechnology and Analytical Chemistry, Sept 2008 Crib

1) Nanotechnology proves that size does matter. To have a sense on the scale of nanoscience, please give approximate data for the following items in unit of nm:

(i) length of C-C bond;

Sub-nanometer (0.154nm)

(ii) diameter of a DNA double helix;

nanometer scale (2 nm)

(iii) size of human red blood cell;

Micrometer scale (7,000 nm)

(iv) diameter of buckyball (C60);

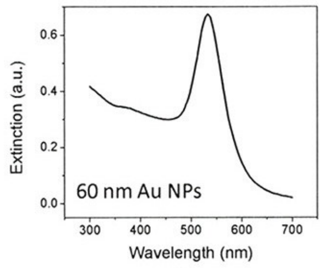
nanometer scale (1nm)

(v) size of a typical virus.

20nm-300 nm scale

2) The Lycurgus glass cup (British Museum, 4th Century AD) has a unique optical property: When illuminated from outside, it appears green. When illuminated with white light from inside, it glows red. It is known the cup contains gold nanoparticles in the glass. The extinction spectrum of a gold nanoparticle solution is shown below. Please answer the following questions.

Extinction spectrum of 60 nm gold nanoparticle solution.



i. Why does the cup appears green when illuminated from outside? Why does the cup glows red when illuminated from inside?

When illuminated from outside, the gold nanoparticles strongly scatters green light at the Plasmon resonance wavelength (520 nm). When Illuminated from inside, the gold nanoparticles absorbs the green and shorter wavelength light, thus the cup appears red.

ii. Sketch an optical device to measure the extinction of a gold nanoparticle solution.

A UV-Vis spectrometer.

iii. For a nanoparticle solution, the extinction is contributed by two physical processes, name the two processes.

The extinction is contributed by absorption and scattering of nanoparticles.

iv. Name two methods to measure the size of these gold nanoparticles.

TEM and Dynamic light scattering

3)

(i) In separation science, the limit of detection (LOD) increases exponentially when the size of analytical column decreases. Accordingly, for HPLC columns with 10-100 um i.d., nanoflow HPLC (10-100 nL/min) is used for the analysis. Please give a rational explanation why nanoflow leads to better LOD than regular flow in HPLC analysis.

(A) Mainly concentration effect. For the same amount of sample (e.g. 1nmol), the concentration is 0.1M for the elution volume of 10 nL and 0.1mM for the elution volume of 10μL.

(B) High surface/volume ratio for small stationary phase particles, which leads to high separation efficiency.

(ii) Electrospray ionization (ESI) is the interface between reverse phase liquid chromatography and mass spectrometer. Nano-electrospray (commonly called nanospray) disposes 10-100 nL of solution per min and is used with high sensitivity in the analysis of complex biological samples. Please explain the high sensitivity of nanospray ionization compared to regular ESI.

(A) Highly efficient desolvation in nanospray which leads to high ionization efficiency.

(B) Concentration effect.

4) TiO_2 and ZnO can absorp a broad spectrum of UV lights and such property have been applied as personal care products. The use of TiO2 and ZnO nanoparticles is probably one of the earliest applications of nanomaterials in commercial use. However, their benefits and potential risk to human health represent a typical example under heated debate on the development of nanomaterials for wide applications in daily life.

i) Make your argument using TiO_2 and ZnO nanoparticles whether nanomaterials should or should NOT be used in health products.

(A) If you favor it, you need to state the advantage of using nano TiO2 and ZnO particles for "transparent" sunblock. Regular size TiO2 and ZnO will deflect all light and give sunblock white color.

(B) If you are against it, you need to state that nano size TiO2 and ZnO could absorb UV light and then permeate cells, leading to potential DNA damages.

ii) Propose one method to map the distribution these nanoparticles in the skin tissue.

Examples include non-linear optical spectroscopy, EM, confocal microscope (after proper labeling) etc.

9/20/08

INORG Cumulative Exam KEY

1. $H_3NBH_3 \longrightarrow [HNBH] + 2H_2$

15 $\dfrac{4\ g\,mol^{-1}}{(6+14+11)\ g\,mol^{-1}} = 12.9\%$

$H_3C\,NH_2\,BH_3 \longrightarrow [H_3CNBH] + 2H_2$

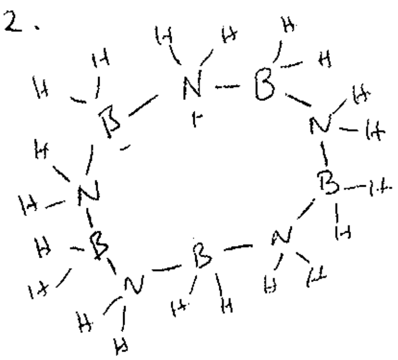
$\dfrac{4\ g\,mol^{-1}}{(15+5+14+11)\ g\,mol^{-1}} = 8.89\%$

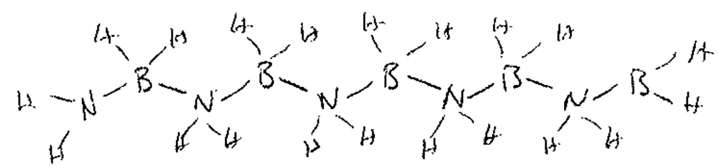
$H_2O \longrightarrow H_2 + [O]$

$\dfrac{2\ g\,mol^{-1}}{(2+16)\ g\,mol^{-1}} = 11.1\%$

2.

10





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15 3. Easier to remove from the gas (fuel) tank & transport for recycling off board.

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10 4. Steric reasons, with an additional Me it is a bulkier substrate.

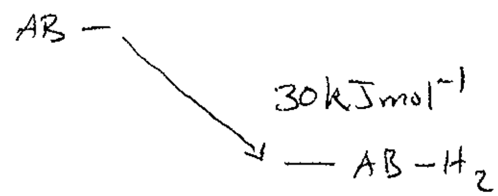
5. Once AB or MeAB is dehydrogenated the products are sufficiently down hill in energy that regeneration under mild conditions is not feasible.

Dehydrogenation is ca. -7 kcal mol^{-1} (-29 kJ mol^{-1})

20 @ ambient temp $RT = 8.3145\ J\,mol^{-1}K^{-1} \times 298K$

$\cong 2.5\ kJ\,mol^{-1}$

Too steep to climb out of under mild conditions



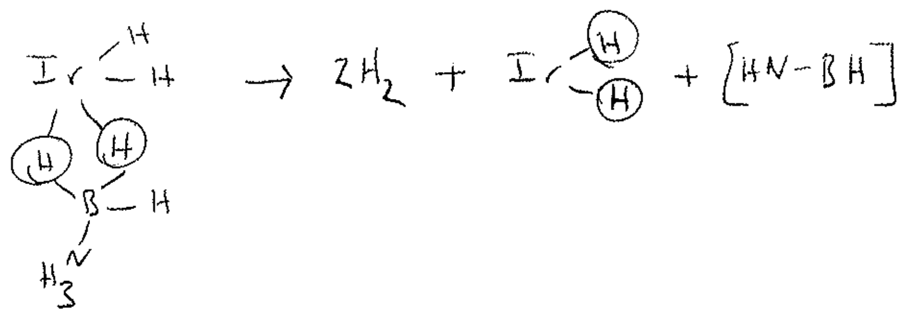
6. Ir is very expensive. The ligand is very expensive.

15 Product is not soluble

The kinetics are slow. Cat. conc. are too high for practical use.

7.

15



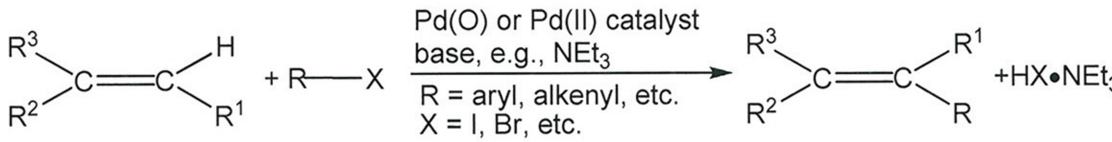
+ Other alternative pathways.

Organic Cumulative Examination 100/100

Name: Crib

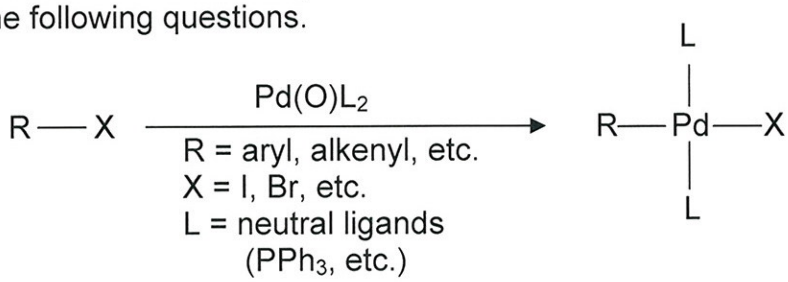
September, 2008

[1] The Heck reaction involves a Pd-catalyzed C-C bond formation between an alkene and an unsaturated organic halides, as shown in Eq. 1.



Eq. 1

This reaction is considered to proceed via a series of concerted processes. Given that the initial microstep is an **oxidative addition** reaction shown in Eq. 2, answer the following questions.



Eq. 2

Note: There may be more than one correct answer.

(i) (4 pts.) What is **oxidized** in Eq. 2? Circle all correct answers.

(a) R—X
(b) PdL_2
(c) R
(d) X

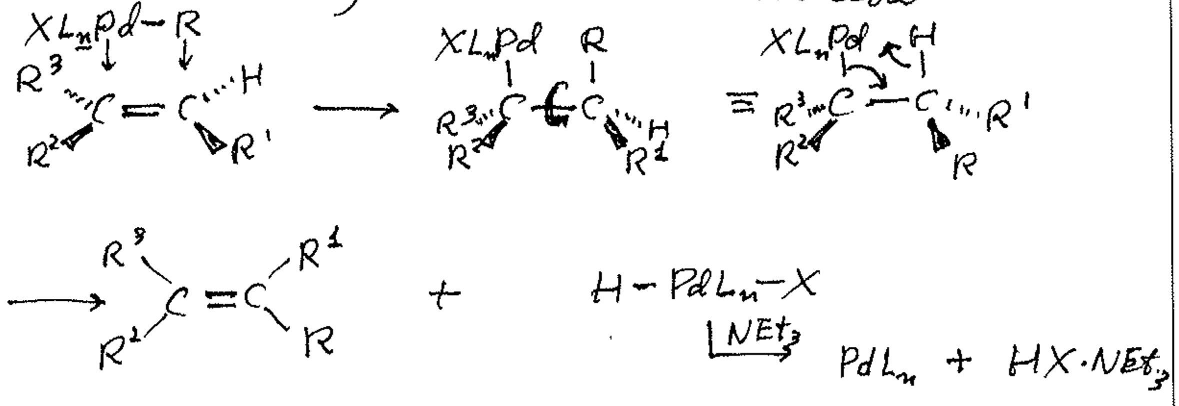
(ii) (4 pts.) What is **reduced** in Eq. 2? Circle all correct answers.

both →
(a) R—X
(b) PdL_2
(c) R
(d) X

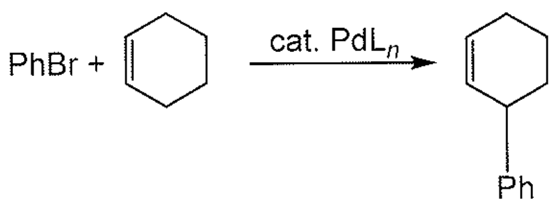
(iii) (8 pts.) The reaction shown in Eq. 1 suffers from an alkene stereochemical inversion. Show a plausible concerted process that clearly explains the indicated stereoinversion.

Your answer must be shown below (not in a separate book).

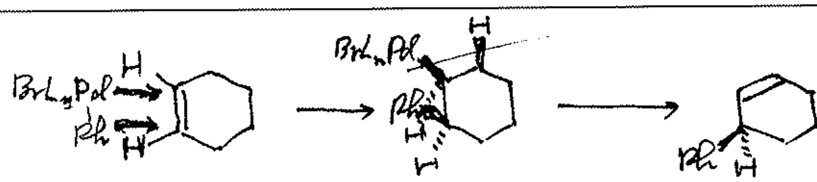
The Heck reaction proceeds via syn C—Pd bond addition and syn H—Pd elimination



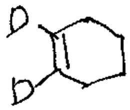
(iv) (8 pts.) The Heck reaction of cyclohexene involves substitution of an allylic C—H bond with the R group of RX. Write a plausible mechanistic scheme consistent with the observed fact(s) shown in Eq. 3.

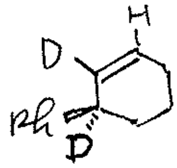


Eq. 3



(v) (8 pts.) Discuss very briefly how you might provide support for your mechanism.

If  is used, the following dideuterio isomer should be formed.



Any other sensible answer is acceptable.

[2] (8 pts.) Select two main reasons for using d-block transition metals in organic synthesis **that are not readily shared by other classes of elements**. Circle the correct **two**.

(a) Ability to provide Lewis acidic site(s).

(b) Ability to provide Lewis basic site(s).

(c) Ability to be readily oxidized and reduced.

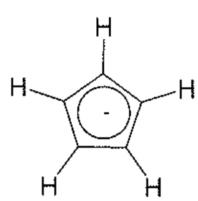
(d) Ability to be readily oxidized and reduced under one set of reaction conditions in one pot.

(e) Ability to provide simultaneously both Lewis acidic and Lewis basic sites.

(f) Ability to provide simultaneously both Lewis acidic and Lewis basic sites as sustainable (thermally stable) and readily regeneratable species.

(g) Ability to serve as radical sources.

[3] Cp_2MCl_2, where M = Ti, Zr, or Hf, can serve as useful catalysts for organic transformations. Answer the following questions by filling the answer boxes.

Cp_2MCl_2 Cp^- =  = 6 e^- ligand

M = Ti, Zr, or Hf.

(i) (4 pts.) The formal oxidation state of M is +4.

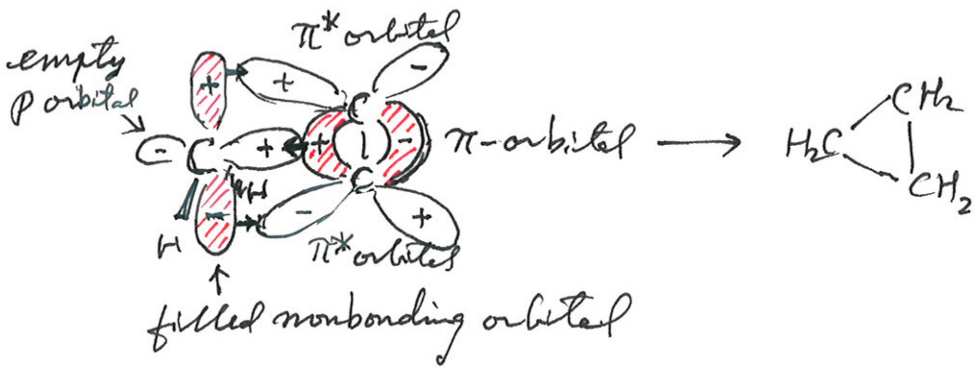
(ii) (8 pts.) Cp_2MCl_2 is considered to be a 16 -electron species with 1 empty valence shell orbital(s).

(iii) (4 pts.) In a hypothetical species "Cp_2M", where M = Ti, Zr, or Hf, the formal oxidation state of M is +2 .

(iv) (12 pts.) "Cp_2M" is considered to be a 14 -electron species providing 2 empty and 1 filled nonbonding valence-shell orbitals.

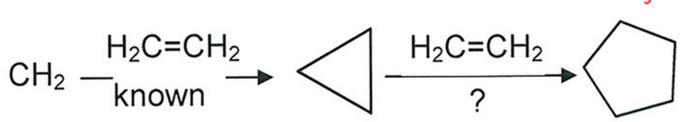
(v) (4 pts.) Singlet methylene (CH_2), a carbenoid species, is a 6 -electron species providing a pair of empty and filled nonbonding valence-shell orbitals and is hence capable of readily reacting with ethylene and other alkenes to give cyclopropanes.

(vi) (8 pts.) Show in the box below how the two frontier orbitals interact with the π and π^* orbitals of ehtylene to give cyclopropane. Make sure to clearly distinguish empty orbitals from doubly occupied orbitals by shading the latter and show orbital symmetry by using + and - signs.



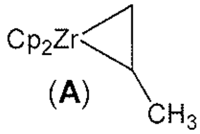
(vii) (4 pts.) Can you expect the product cyclopropane to react further with the second molecule of ethylene to give cyclopentane? readily?

Answer: Yes ☐ or ☑ No not readily.

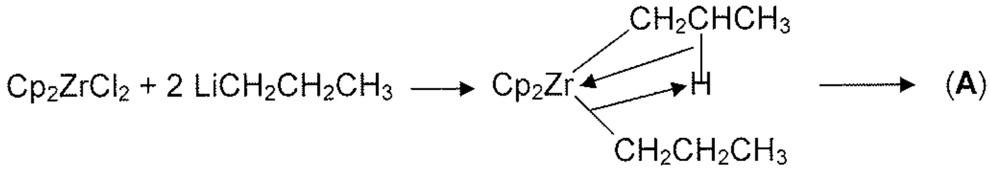


(viii) (8 pts.) If your answer is "Yes", show an orbital interaction diagram similar to what is shown in (v). If "No", explain very briefly in less than 20 words why.

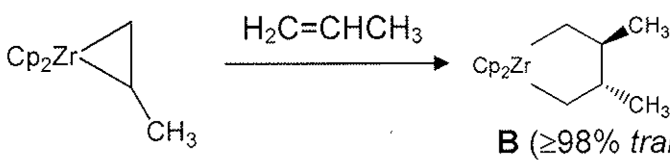
Although strained, cyclopropane is a coordinatively saturated compound in which all 3 C atoms are octets and Hs are duets. Without any valence shell empty orbital, cyclopropane cannot readily react with the second molecule of ethylene.

(ix) (8 pts.) Treatment of Cp_2ZrCl_2 with 2 equivalents of ^nPrLi initially gives $Cp_2Zr(CH_2CH_2CH_3)_2$ which then undergoes an intramolecular β-H abstraction to provide 

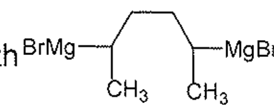
(**A**)

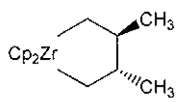


(**A**) can react with $H_2C{=}CHCH_3$ to give (**B**)

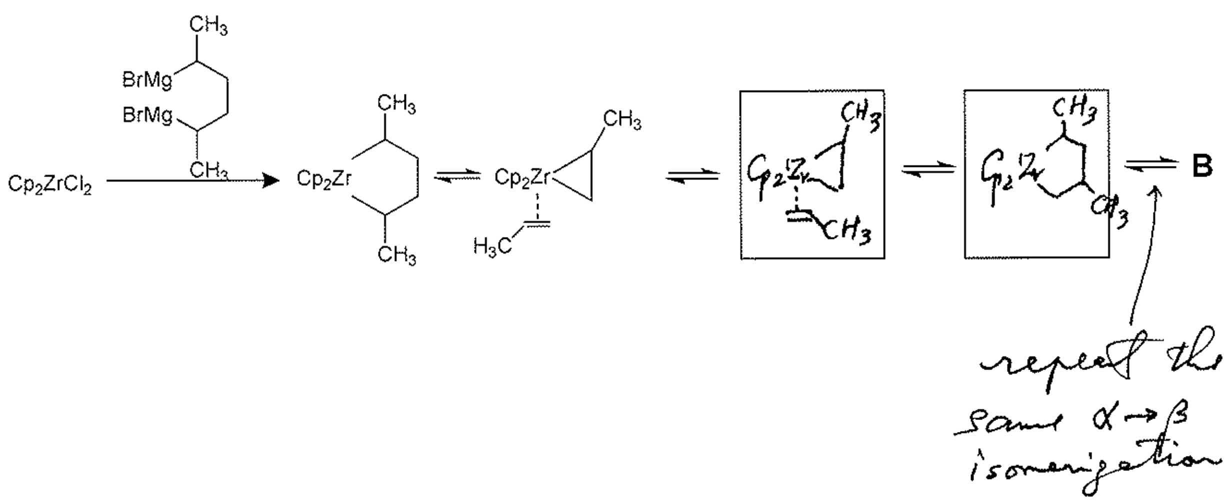


B (≥98% *trans*)

Interestingly, treatment of Cp_2ZrCl_2 with 

gives clearly 

which is also ≥98% *trans*. Complete the following mechanistic scheme which has been supported by NMR analyses of the corresponding reaction of Cp_2HfCl_2 (*CC* **1990**, 182). The NMR analyses suggest that the entire process can be and is at least predominantly intramolecular.



Physical Chemistry Cume Sept 20, 2008

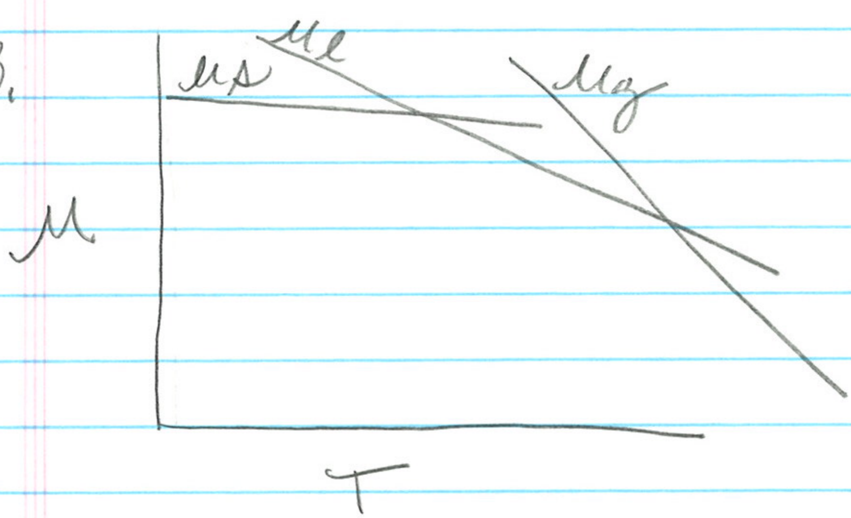
1A. $dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$

1B. $dG = -S\,dT + V\,dP$

$-S = \left(\frac{\partial G}{\partial T}\right)_P \qquad V = \left(\frac{\partial G}{\partial P}\right)_T$

2. $\mu = \frac{G}{n} \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S$ so $\left(\frac{\partial \mu}{\partial T}\right) = -S_m = -\frac{S}{n}$

3.



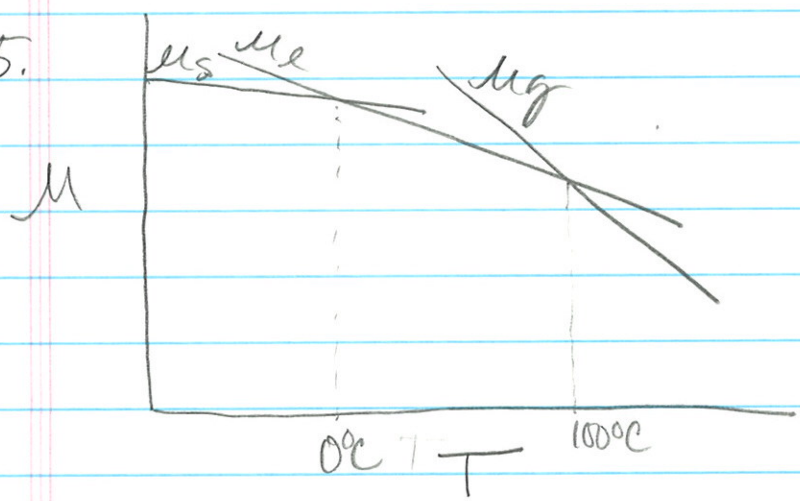
I. The slopes are all negative $slope_s < slope_l << slope_g$

II Because the slope is given by $\left(\frac{\partial \mu}{\partial T}\right) = -S_m$

the molar entropy of a gas is much larger than a liquid which is larger than the molar entropy of a solid.

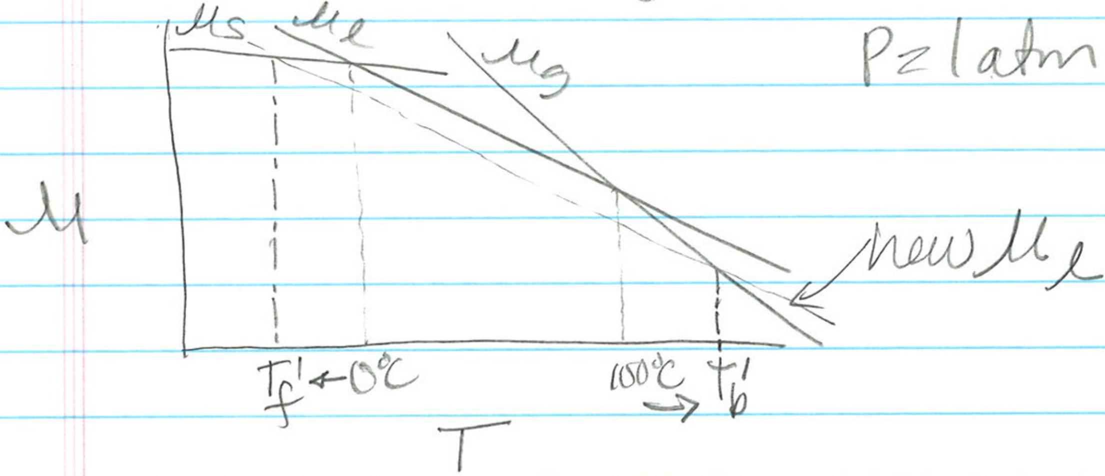
4. The most stable phase at a specific P & T has the lowest chemical potential.

5.



P=1atm

6. The chemical potential of the liquid water decreases, which lowers the freezing pt & raises the boiling pt.



P=1atm

7. A) $\mu_{liq} = \mu_{vapor}$ Raoult's law $p = p^0 X$

$= \mu^0_{vapor} + RT\ln p$

$= \mu^0_{vapor} + RT\ln p^0_{solvent} + RT\ln x_{solvent}$

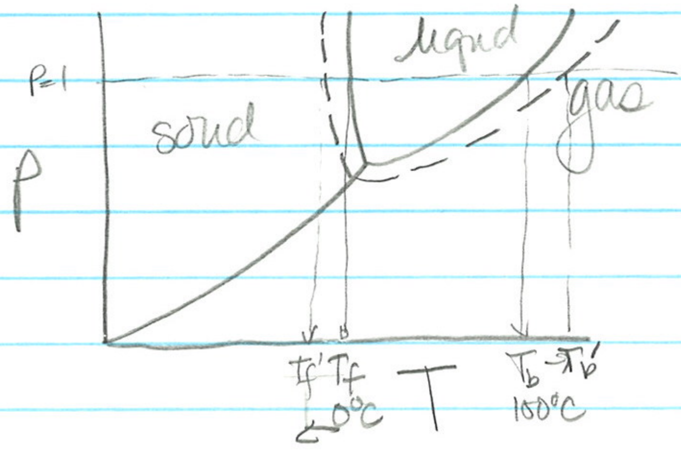
Recall for pure l $\mu^0_l = \mu^0_v + RT\ln p^0_{solvent}$

$$\boxed{\mu_{liq} = \mu^0_{liq} + RT\ln X_{solvent}}$$

B. $X_{solvent} < 1$, so $\ln x_{solvent} < 0$, thus the chemical potential of the liquid in a solution is less than the chemical potential of pure liquid.

C. Thats why the $\mu_{solvent}$ is drawn BELOW the μ_l.

8.



The s-l line moves and the l-g line moves the s-g does not. FP↑, BP↓