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Lectures 20-21
Chemistry 163B W2020
Multicomponent Phase Rule
*and Solution Behavior*

1

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le menu

➢ phase rule for multicomponent systems

➢ solid A-solid B phase diagram

➢ ideal solutions

➢ solution-vapor phase diagrams

➢ fractional distillation and vapor diffusion crystal growth

2

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phase rule (lectures 18-19)

1 component   P

$f = 3\text{-}p$

T

1 phase: T,P vary independently
2 phases present: T and P covary
3 phases present: fixed T and P

3

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multi-component phase rule $f = 2 + c - p$ *f=3-p for c=1*

- c = number of components (molecular species)
  p= number of coexisting phases
- *intensive* variables required to specify system
  T, P, $X_i^{(\alpha)}$ (mole fraction of component i in phase α)
- total variables to specify
  total vars=2 + (c-1) p
  [2 from T,P; (c-1) independent mole fractions in each phase]
- total restrictions for equilibrium
 total restrictions = c (p-1)
  [already T, P same in each phase]

  set $\mu_i^{(\alpha)}$ *then* $\mu_i^{(\alpha)} = \mu_i^{(\beta)} = \ldots \mu_i^{(p)}$ *(p - 1 restrictions for each component)*
  $c(p-1)$ *total restrictions for c components*

- f = total variables – total restrictions
     T,P $X_i^{(\alpha)}$ $\mu_i^{(\alpha)} = \mu_i^{(\beta)} \ldots$
- $f = 2 + (c\text{-}1) \, p \; - c \, (p\text{-}1) = \boxed{2 + c \text{ - } p}$

4

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phase rule and Cd-Bi phase diagram (P=1 atm)

- f=2+c-p
- c=2 (Bi, Cd)
- f=4-p
- set P=1atm
- $f_{remaining}$=3-p
- variables:
  T, χ_{Cd}^ℓ in liquid

P= 1 atm
Atomic Percent Cadmium

L

liquid

liq+ Bi(s)   liquid + Cd(s)

Cd (s) +Bi (s)

$"\chi_{Cd}^\ell \;"\rightarrow$

5

Listen up!!!

**UNDERSTAND THE FOLLOWING DISCUSSION
OF THE PHASE RULE AND THIS
BINARY COMPONENT PHASE
DIAGRAM**

it may be very good for your future   **happiness**

6

1

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phase rule and Cd-Bi phase diagram (P=1 atm)

- f=2+c-p
- c=2
- f=4-p
- set P=1atm
- $f_{remaining}$=3-p
- variables: T, χ^ℓ_{Cd}

liquid,
p=1, f=2
T, χ^ℓ_{cd} can vary

solid < 146° C,
p=2, f=1
T can vary
note: Cd(s)
  and Bi(s) are
  pure solids,
  not solution (alloy),
χ^s_{cd}=1 χ^s_{Bi}=1

m.p. of pure Bi= 271.4°C
m.p. of pure Cd= 321.1°C

7

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phase rule and Cd-Bi phase diagram (P=1 atm)

- $f_{remaining}$=3-p
- variables: T, χ^ℓ_{Cd}

+ total mole fraction Cd

T < 280°C
liquid + Cd(s),
p=2, f=1
only T or χ^ℓ_{cd} can independently
vary (i.e. T and χ^ℓ_{cd} covary)

Cd(s)
just appears

liquid + Cd(s)

Cd(s)

lower T χ^{total}_{Cd} fixed

- T≈ 340°C [liquid $X_{Cd}^{(\ell)}$=$X_{Cd}^{(total)}$]
- T≈ 280°C [liquid +Cd(s) begins to appear]
- T≈ 250°C [$X_{Cd}^{(\ell)}$ decreases, as more Cd(s)]
- T≈ 185 °C [$X_{Cd}^{(\ell)}$ decreases, more Cd(s)]

8

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phase rule and Cd-Bi phase diagram (eutectic)

$f_{remaining}$=3-p

liquid +Cd(s) + Bi(s)
p=3, f=0
T and χ^ℓ_{cd}
fixed
T=146° C,
χ^ℓ_{Cd}=0.55
=0.39 wt%

Bi(s)
just appears

liq+ Bi(s)

liquid + Cd(s)

Cd(s)
just appears

Cd (s) +Bi (s)

eutectic=constant freezing composition (mixture)

9

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not all solid-solid mixtures form eutectics

$NaAlSi_3O_8 + CaAl_2Si_2O_8$ Cu   +   Ni

10

Ideal Solutions

11

Molecular Basis for Ideal Sol'ns.

- In pure liquid A, there are only **A-A** interactions.
- In pure liquid B, there are only **B-B** interactions.
- In solutions of A and B, there are **A-B** interactions as well.
- ΔH_{mixing}= 0
  means that all three interactions are of equal strength.

12

2

ideal solutions

properties of the solution depend only on the properties of components in bulk (pure) and the mole fractions of the components.

for example partial vapor pressure of components:

mole fraction A in liquid ────

$P_A^{(v)} = X_A^{(l)} P_A^{\bullet}$ ──── vapor pressure of pure A

$P_B^{(v)} = X_B^{(l)} P_B^{\bullet}$ ──── vapor pressure of pure B

$$P_{total} = P_A^{(v)} + P_B^{(v)} = X_A^{(l)} P_A^{\bullet} + X_B^{(l)} P_B^{\bullet}$$
$$= X_A^{(l)} P_A^{\bullet} + \left(1 - X_A^{(l)}\right) P_B^{\bullet}$$
$$= X_A^{(l)} \left(P_A^{\bullet} - P_B^{\bullet}\right) + P_B^{\bullet} \quad \text{──── linear } P_{total} \text{ vs } X_A^{(l)}$$

correction for non-ideality
activity
HW #7 prob 55

$$P_i^{(v)} = a_i^{(l)} P_i^{\bullet}$$
$$ideal \; a_i^{(l)} = X_i^{(l)}$$
$$non-ideal \quad a_i^{(l)} = \gamma_i^{(l)} X_i^{(l)}$$

13

$liq \leftrightarrow vap$ Eq. in Binary Mixtures

- Both the liquid and the vapor phase are binary mixtures of A and B.
- x_A, x_B are the mole fractions in the liquid.
- y_A, y_B are the mole fractions in the vapor.
- p_A, p_B are the partial pressures in the vapor.

http://classweb.gmu.edu/sdavis/chem331/engel9x.ppt
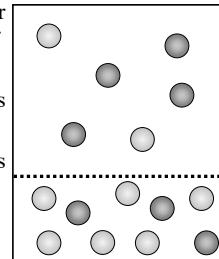
14

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benzene-toluene, quite ideal (similar to Fig 9.2 E&R4th) !!

$$P_{total} = X_A^{(l)} \left(P_A^{\bullet} - P_B^{\bullet}\right) + P_B^{\bullet}$$

Benzene and Toluene

http://www.chem.ucsb.edu/coursepages/06fall/1C-Watts/dl/Lecture_Notes/Lecture16.%2011-8-06Colligative%20Properties%20Solutions.pdf
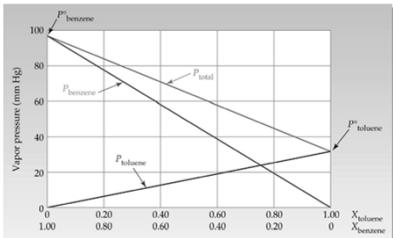
15

Ethyl Acetate/Acetic Anhydride

p /torr

(4 torr)

$X_{ethyl \; acetate}$

http://classweb.gmu.edu/sdavis/chem331/engel9x.ppt
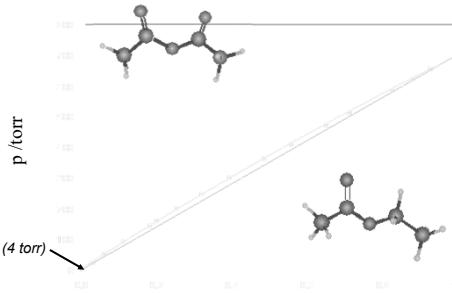
16

$X^{(l)}$ vs $X^{(v)}$ (notation conventions)

conventions:

mole fraction liquid component A:

$X_A^{(l)}$ or $X_A^{(solution)}$ most descriptive;
     but also X_A (sloppy) and $x_1(E\&R)$

mole fraction gas (vapor) component A:

$X_A^{(v)}$ most descriptive;
     but also $y_1(E\&R)$ [not very descriptive and weird??;
                but note for E&R HW probs]

17

$X^{(l)}$ vs $X^{(v)}$

relate $X^{(l)}$ vs $X^{(v)}$ assuming vapor is ideal gas

$$P_{total} = P_A + P_B = n_{total}^{(v)} \frac{RT}{V}$$

$$P_A = n_A^{(v)} \frac{RT}{V} \quad P_B = n_B^{(v)} \frac{RT}{V}$$

$$\frac{P_A}{P_{total}} = \frac{n_A^{(v)}}{n_{total}^{(v)}} = X_A^{(v)} \quad and \quad \frac{P_B}{P_{total}} \frac{n_B^{(v)}}{n_{total}^{(v)}} = X_B^{(v)}$$

$$P_A = X_A^{(l)} P_A^{\bullet} \quad or \quad P_A = \gamma_A X_A^{(l)} P_A^{\bullet}$$

$$\boxed{X_A^{(v)} = \frac{P_A}{P_{total}} = \frac{X_A^{(l)} P_A^{\bullet}}{P_{total}}} \; (E\&R\text{'s } y_A)$$

HW#7 probs 50, 55 use E&R's y_i

18

3

how does $\mu^{(v)}$ relate to $X^{(\ell)}$? ($\gamma_i^{(v)} = 1$ *for* ideal gas; $\gamma_i^{(\ell)} = 1$ *for* ideal solution)

$$\mu_i^{(\ell)} = \mu_i^{(v)} \text{ for each component } i \text{ in mixture}$$

$$\mu_i^{(v)}(T,P,X_i^{(\ell)}) = \mu_i^{s(v)}(T) + RT\,ln(\underbrace{\gamma_i^{(v)}P_i^{(v)}(T)/1\,bar})$$
$$f_i$$

$$\mu_i = \mu_i^s + RT\,ln\left[\frac{P_i}{1\,bar}\right] \text{ old stuff !!}$$

$$P_i^{(v)} = \gamma_i^{(\ell)}X_i^{(\ell)}P_i^{*(v)}$$

$$\mu_i^{(v)}(T,P,X_i^{(\ell)}) = \mu_i^{s(v)}(T) + RT\,ln(\gamma_i^{(v)}P_i^{*(v)}(T)/1\,bar) + RT\,ln(\gamma_i^{(\ell)}X_i^{(\ell)})$$

$$\underbrace{\qquad\qquad\qquad\qquad}$$
$$\boxed{\mu_i^{*(v)}(T,P_i^*)}$$
chemical potential of pure component i

$$\boxed{\mu_i^{(v)}(T,P,X_i^{(\ell)}) = \mu_i^{*(v)}(T,P_i^*) + RT\,ln(\gamma_i^{(\ell)}X_i^{(\ell)})}$$

19

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a little more of how does $\mu^{(\ell)}$ relate to $X^{(\ell)}$?

$$\mu_i^{(v)}(T,P,X_i^{(\ell)}) = \mu_i^{*(v)}(T,P_i^*) + RT\,ln(X_i^{(\ell)}) \text{ ideal soln } \gamma_i^{(\ell)}=1$$

solution ⇌ vapor components in equilibrium at T
$$\mu_i^{(\ell)}(T,P,X_i^{(\ell)}) = \mu_i^{(v)}(T,P,X_i^{(\ell)})$$

pure liquid ⇌ pure vapor components in equilibrium at T
$$\mu_i^{*(\ell)}(T,P_i^*) = \mu_i^{*(v)}(T,P_i^*)$$

we get

$$\boxed{\mu_i^{(\ell)}(T,P,X_i^{(\ell)}) = \mu_i^{*(\ell)}(T) + RT\,ln(X_i^{(\ell)}) \quad \text{ideal solution}}$$

$$\mu_i^{(\ell)}(T,P,X_i^{(\ell)}) = \mu_i^{*(\ell)}(T) + RT\,ln(\underbrace{\gamma_i^{(\ell)}X_i^{(\ell)}}) \quad \begin{array}{c}\text{corrected for}\\\text{nonideality}\end{array}$$
$$a_i$$

20

Ideal Solutions

from: https://switkes.chemistry.ucsc.edu/teaching/CHEM163B/HANDOUTS/ideal_soln_thermo.pdf

Handout #50

I. The partial molar volume of each component in solution is the same as its molar volume in pure liquid and thus the volume of the solution is the additive volume of the pure components

$$\bar{V}_i = \bar{V}_i^{*,\ell} \qquad V = \sum_i n_i \bar{V}_i$$

II. The enthalpy of mixing is zero: $\Delta H_{mix} = 0$

III. The free energy of mixing is: $\Delta G_{mix} = \sum_k n_k RT\ln X_k^{\ell}$

IV. The entropy of mixing is: $\Delta S_{mix} = \dfrac{\Delta H_{mix} - \Delta G_{mix}}{T} = -\sum_k n_k R\ln X_k^{\ell}$

21

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it may be very good for your future   **happiness**

22

T vs X (P=1 atm) for solution-vapor equilibrium TOLUENE + BENZENE

toluene (b.p.=383.78) + benzene (b.p.=353.25)

vapor composition

tol+ben (vapor)
[$f_{remaining}$=2]

solution + vapor
[$f_{remaining}$=1]

solution composition
tol+ben (solution)
[$f_{remaining}$=2]
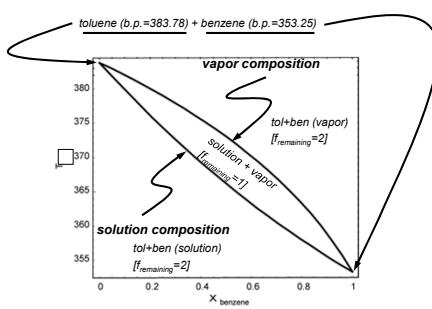
23

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fractional distillation [T_{bp} vs $(X_{benzene})^{solution}$]

$$T_{bp}\left(X_{benzene}^{soln}\right)$$

- $\ln\left(\dfrac{P_{benzene}^*(T)}{1\,atm}\right) = \dfrac{(\Delta \bar{H}_{vap})_{ben}}{R}\left[\dfrac{1}{T} - \dfrac{1}{(T_b^*)_{ben}}\right]$
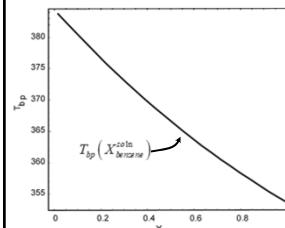
- $\dfrac{P_{benzene}^*(T)}{1\,atm} = e^{\frac{(\Delta \bar{H}_{vap})_{ben}}{R}\left[\frac{1}{T}-\frac{1}{(T_b^*)_{ben}}\right]}$ vapor pressure of benzene at T

- $\dfrac{P_{toluene}^*(T)}{1\,atm} = e^{\frac{(\Delta \bar{H}_{vap})_{tol}}{R}\left[\frac{1}{T}-\frac{1}{(T_b^*)_{tol}}\right]}$ vapor pressure of toluene at T

- in ideal solution
  $P_{benzene}(T) = X_{benzene}^{solution}P_{benzene}^*(T)$ and $P_{toluene}(T) = X_{toluene}^{solution}P_{toluene}^*(T)$

- at boiling ⇒ $P_{benzene} + P_{toluene} = 1$ atm
  $1\,atm = X_{benzene}^{solution}P_{benzene}^*(T_{bp}^{solution}) + (1-X_{benzene}^{solution})P_{toluene}^*(T_{bp}^{solution})$

- for a given $X_{benzene}^{solution}$ solve for $T_{bp}^{solution}$
  (or better have Mathematica solve equations
  see handout #51)

24

Slide 25

fractional distillation [T_{bp} vs ($X_{benzene}$)^{vapor}]

$T_{bp}\left(X_{benzene}^{vapor}\right)$

$$X_{benzene}^{vapor} = \frac{P_{benzene}}{P_{total}} = \frac{X_{ben}^{soln} P_{ben}^{\bullet}(T_{bp}^{solution})}{P_{total}}$$

$$X_{benzene}^{vapor} = X_{ben}^{soln} P_{ben}^{\bullet}(T_{bp}^{solution})$$

since $P_{total} = 1\ atm\ at\ T_{bp}^{solution}$

get $T_{bp}^{solution}$ from equations on previous slide

25

Slide 26

two-phase region (P=1 atm) TOLUENE + BENZENE ($\ell \rightleftarrows v$)

at 365K a mixture of total X_b=.70
will be a liquid X^{ℓ}_b=.55 in equilibrium
with vapor X^v_b=.76

solution + vapor

● liquid
○ vapor
★ total

.55 .70 .76 TIE-LINE

26

Slide 27

T vs X (P=1 atm) for solution-vapor equilibrium TOLUENE + BENZENE

toluene (b.p.=383.78) + benzene (b.p.=353.25)

$$X_{benz}^{total} = 0.65$$

vapor composition

solution composition

solution + vapor
[$f_{remaining}$=1]   [$f_{remaining}$=2]

tol+ben (vapor)

tol+ben (solution)
[$f_{remaining}$=2]

- a solution of $X_{benz}^{(\ell)} \approx 0.65$ at T=357K is a liquid
- that boils at ~362K (P_{total}=1atm)
- at T ~362K the soluton is in equilibrium with vapor $X_{benz}^{(v)}$ =.83
- if the system is maintained at P_{total} =1 atm and T is raised to 365K, liquid will evaporate until $X_{benz}^{(\ell)}$=0.53 and $X_{benz}^{(v)}$=0.74
- above T=369.8K the system is all vapor with X_{benz}^v =0.65

● liquid
○ vapor
★ total

27

Slide 28

fractional distillation

thermometer
Cold water out
Fractional Distillation
in the Laboratory
fractionating column
liebig condenser
blue liquid boils at 80°C
cold water in
homogeneous mixture of liquids
distillate
anti-bumping granules
HEAT

http://www.wpbschoolhouse.btinternet.co.uk/page12/gifs/FracDistRed.gif

etc !!

v_3
ℓ_3
T_3 $X_3^{(\ell)} = X_2^{(v)}$

v_2
ℓ_2
T_2 $X_2^{(\ell)} = X_1^{(v)}$

v_1
ℓ_1
T_1

$T_1 > T_2 > T_3$

28

Slide 29

fractional distilation

toluene (b.p.=383.78) + benzene (b.p.=353.25)
benzene more "volatile" than toluene

vapor composition

solution composition

II
I
III
IV

top of column (cooler)

VI. approaches $X_{benzene}$=1

V. etc, ...

IV. ● evaporate
   • vapor $X^v_{benzene} \approx$.88

III. ● condense $X^{soln}_{benzene} \approx$.72
    • $T_{bp} \approx$359.5

II. ● vapor $X^v_{benzene} \approx$.72

I. ● start with 50-50 mixture
   • $T_{bp} \approx$ 366

bottom of column (warmer)

29

Slide 30

azeotrope (non-ideal solution)

Vapor
Liquid
Constant-boiling azeotrope
Mole fraction benzene
Ethanol
Benzene

• fractional distillation leads to constant boiling azeotrope in vapor

•and (in pot after azeotrope boils off)
 • $(X_A)_{initial} > (X_A)_{azeotrope}$ pure A
 • $(X_A)_{initial} < (X_A)_{azeotrope}$ pure B

vapor
Liquid
Composition

http://www.solvent--recycling.com/azeotrope_1.html

30

5

fractional distillation

http://home.att.net/~cat6a/images/fuels_06.gif

31

vapor diffusion crystal growth

H_2O (vap)

conc KCl

crystallization from semi-saturated protein

32

Vapor Diffusion Crystal Growth

Protein Crystal Growth

http://science.nasa.gov/ssl/msad/pcg/#HARDWARE

33

End of Lecture 20-21

34

$\mu_i^{(\ell)} = \mu_i^{(v)}$ for each component i

have proven $\mu_A^{(\ell)} = \mu_A^{(v)}$ single component A

$$dG = -SdT + VdP + \sum_j \mu_j dn_j$$

$$dG = -SdT + VdP + \sum_{i,\omega} \mu_i^{(\omega)} dn_i^{(\omega)}$$

← ω^{th} phase
← i^{th} component

at equilibrium

$$dG_{T,P} = 0 = \sum_{i,\omega} \mu_i^{(\omega)} dn_i^{(\omega)}$$

for each component i $\ell \rightleftarrows v$ $dn_i^{(v)} = -dn_i^{(\ell)}$

$$\sum_{i,\omega} \mu_i^{(\omega)} dn_i^{(\omega)} = 0 \Rightarrow \sum_i \left(\mu_i^{(\ell)} - \mu_i^{(v)} \right) dn_i^{(\ell)} = 0 \Rightarrow \boxed{\mu_i^{(\ell)} = \mu_i^{(v)}} \text{ for each component}$$

35

relative amounts of components in two-phase region

relative amount: $\dfrac{n_{vapor}}{n_{solution}} = \dfrac{L_{soln}}{L_{vap}}$

$(L_{vap}=0)$ all vapor $\dfrac{n_{solution}}{n_{vapor}} = \dfrac{L_{vap}}{L_{soln}}$

$(L_{soln}=0)$ all solution $\dfrac{n_{vapor}}{n_{solution}} = \dfrac{L_{soln}}{L_{vap}}$

36

6

Cd-Bi phase diagram (eutectic) Cd(s)+Bi(s)⇄liquid is straight line T=146°C

Atomic Percent Cadmium

eutectic $\mu_{Cd}(\chi^\ell_{Cd}=0.55, T=146°C)=\mu_{Cd}(s, T=146°C)$

$\mu_{Bi}(\chi^\ell_{Bi}=0.45, T=146°C)=\mu_{Bi}(s, T=146°C)$

ℓ

liq+ Bi(s)

liquid + Cd(s)

146°C

(Bi)

(Cd)

Cd (s) +Bi (s)

T>146C°
③ Cd-Bi (X_{Cd})=.55

T=146C°
② Cd (s) +Bi (s)
↑↓
Cd-Bi (X_{Cd})=.55

T<146C°
① Cd (s) +Bi (s)

"χ^ℓ_{Cd}"→ $X^{total}_{Cd}=.55$

37

Cd-Bi phase diagram (eutectic) Cd(s)+Bi(s)⇄liquid is straight line T=146°C

Atomic Percent Cadmium

eutectic $\mu_{Cd}(\chi^\ell_{Cd}=0.55, T=146°C)=\mu_{Cd}(s, T=146°C)$

$\mu_{Bi}(\chi^\ell_{Bi}=0.45, T=146°C)=\mu_{Bi}(s, T=146°C)$

ℓ

liq+ Bi(s)

liquid + Cd(s)

Bi(s)

eutectic

146°C

(Bi)

(Cd)

Cd (s) +Bi (s)

T>≈225°C
③ Cd-Bi (X_{Cd})=.2

T=146°C (first liquid)
Bi (s) *remaining Bi(s)*
② ↑↓
Cd-Bi (X_{Bi})=.45
all of Cd, some of Bi

T<146°C
① Cd (s) +Bi (s)

$X^{total}_{Cd}=.2$
$X^{total}_{Bi}=.8$

"χ^ℓ_{Cd}"→

38

Cd-Bi phase diagram (eutectic) Cd(s)+Bi(s)⇄liquid is straight line T=146°C

Atomic Percent Cadmium

eutectic $\mu_{Cd}(\chi^\ell_{Cd}=0.55, T=146°C)=\mu_{Cd}(s, T=146°C)$

$\mu_{Bi}(\chi^\ell_{Bi}=0.45, T=146°C)=\mu_{Bi}(s, T=146°C)$

ℓ

liq+ Bi(s)

liquid + Cd(s)

146°C

eutectic

146°C

Cd(s)

(Bi)

(Cd)

Cd (s) +Bi (s)

T>≈280°C
③ Cd-Bi (X_{Cd})=.8

T=146°C (first liquid)
Cd (s) *remaining Cd(s)*
② ↑↓
Cd-Bi (X_{Cd})=.55
all of Bi, some of Cd

T<146°C
① Cd (s) +Bi (s)

$X^{total}_{Cd}=.8$
$X^{total}_{Bi}=.2$

"χ^ℓ_{Cd}"→

39

7