Problem 1

In this problem, there are 3 heat transfer processes: heat generation at the solid/liquid interface, conduction through the droplet, and radiation into the chamber.

1. Compare conduction in the droplet to radiation into the chamber:

$M = \epsilon \, \sigma \, T^3 \, L/k$

For a metal, ϵ = ~0.1; T ~ T_m = 1000 C, k >= 10ish W/m^2K. There are no gradients in the solid for M <= 0.1, so the largest droplet with no gradients is:

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lMax = 0.1 × 10 (0.1 × 5.67 × 10⁻⁸ 1273³)
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11.6968
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Atomization will not involve 11 meter-radius blobs of molten metal, so there will not be gradients in reasonable, small droplets. Therefore, we can neglect conduction in our heat balance.
The rate-limiting step is heat removal via radiation at the droplet surface.

Next, write the heat balance between the heat generated and the radiation:

$Q_{rad} = Q_{gen}$
$A_{rad} \, q_{rad} = A_{gen} \, q_{gen}$

A_{rad} = surface area of the droplet, $4 \, \pi \, R^2$.
A_{gen} = area of the s/l interface, $4 \, \pi \, s^2$.

$q_{rad} = \epsilon \, \sigma \left(T^4 - T_{walls}{}^4 \right)$
$q_{gen} = \rho \, H_f \, ds/dt$

therefore, $R^2 \, \epsilon \, \sigma \left(T^4 - T_{walls}{}^4 \right) = s^2 \, \rho \, H_f \, ds/dt$

Problem 2

Start with the last equation above. Separate variables:
$s^2 \, ds = R^2 \, \epsilon \, \sigma \left(T^4 - T_{walls}{}^4 \right) / (\rho \, H_f) \, dt$

integrate:
$s^3/3 + A = R^2 \, \epsilon \, \sigma \left(T^4 - T_{walls}{}^4 \right) / (\rho \, H_f) \, t$

At t = 0, s = 0, so the integration constant A is zero.
result:
$s = [t \quad 3 \, R^2 \, \epsilon \, \sigma \left(T^4 - T_{walls}{}^4 \right) / (\rho \, H_f)]^{1/3}$

The analog to Chvorinov's rule in this case is $t_{solidify} \propto s^3$

Problem 3

There are many ways to answer this question. The goal of this question was for you to demonstrate that you have thought about when heat transfer steps during solidification are negligable and why.

Three heat transfer processes:
(i) interface resistance. thermal resistivity = 1/h. This is invarient with time.
(ii) conduction through the solid. thermal resistivity = L_s/k_s. This will change with time!
(iii) conduction through the mold. thermal resistivity = L_m/k_m. This is invarient with time.

Processes (i) and (iii) are time-independant. Therefore, only one or the other will matter, you will not have both be important at different times in same problem. Simply compute the Biot number to see what happens: if Bi small, interface resistance is limiting. If Bi is big, conduction through the mold is limiting. If 0.1 < Bi < 10, then both matter, and that is annoying.

Let's look at when Bi is small and interface resistance dominates. A typical refractory material has k ~ 5 W/mK, and we need $h_{sm} L_m/k_m \leq 0.1$, so L_m must be less than 0.1 $(5 \ W/\text{mK}) / (4000 \ W/m^2 \ K) = 125$ μm. Conversely, $L_m \geq 1.25$ cm for conduction in the mold to dominate. Given that molds usually must be strong to support their molten contents, they will probably be cm-scale or thicker. *Thus, if a refractory mold is not actively cooled, it is almost certainly the case that interface resistance is negligable!* This should be comforting, given that we made this assumption in class without justification.

Process (ii) will not matter at t = 0 because L_s = 0, but L_s scales with $\sqrt{t}$, so eventually it will matter. There will be a switch between conduction-limited by the mold to limited by the solid when the ratio if resitsances is between 0.1 and 10: $(L_s/k_s) \ / \ (L_m/k_m) = L_s \ (k_m/L_m \ k_s) \approx L_s$ (5 W/mK) / ((~5 cm) (35 W/mK)) = 2.9 L_s. So, conduction in the mold is rate-limiting when L_s < 0.29m, conduction in the solid is rate-limiting when L_s > 29m, and both contribute for castings in between. Since I can't think of something larger than 29m that we'd cast in a 5cm-thick mold, we can conclude that we never really get to the case of conduction through the solid-limited solidification. *Therefore, conduction through the solid can only be limiting when the mold is actively cooled and the interface resistance is sufficiently small to not be the limiting step.* How small must it be? Bi = $h_{sm} L_s/k_s \geq 10$ for interface resistance to be negligable. If we have a 1m-thick casting, h_{sm} must be greater than or equal to 350 $W/m^2 \ K$. This is quite likely because solid-solid interfaces tend to be ~thousands of $W/m^2 \ K$, it is reasonable to think that solidifcation through the solid can be limiting in a cooled mold.

In short, in a mold that is not actively-cooled, for castings less than 0.1 $L_m \ k_s/k_m$ thick, conduction in the mold is limiting (s $\propto \sqrt{t}$). For thicker castings, both conduction in the solid and in the mold matter (s $\propto$ net effect of the two conductivities, probably goes as $\sqrt{t}$).

In an actively-cooled mold, interface resistance is limiting (s $\propto$ t) until the casting is 10 $k_s/(L_s \ h_{sm})$ thick, at which point conduction through the solid becomes limiting (s $\propto \sqrt{t}$).

Problem 4

A great resource for phase diagrams is the ASM database
(http://www1.asminternational.org/asmenterprise/APD/default.aspx)

The partition coefficient will be constant if the liquidus and solidus are stright lines. If they curve, then c_s and/or c_l will vary with temperature, so k will vary.

Measured at eutectic temperature (for simplicity) off the phase diagrams:

Mg-Al $c_s = 11.1$ at% $c_l = 30.7$ at% $k = c_s/c_l = 0.362$ single value? YES - straight lines
Mg-Li $c_s = 16.7$ at% $c_l = 22.3$ at% $k = c_s/c_l = 0.745$ single value? NO - both are curved
Mg-Y $c_s = 0.7$ at% $c_l = 10.4$ at% $k = c_s/c_l = 0.0673$ single value? NO - solidus is droopy
Mg-Zn $c_s = 2.9$ at% $c_l = 29.2$ at% $k = c_s/c_l = 0.0993$ single value? NO - bulgey liquidus

Problem 5
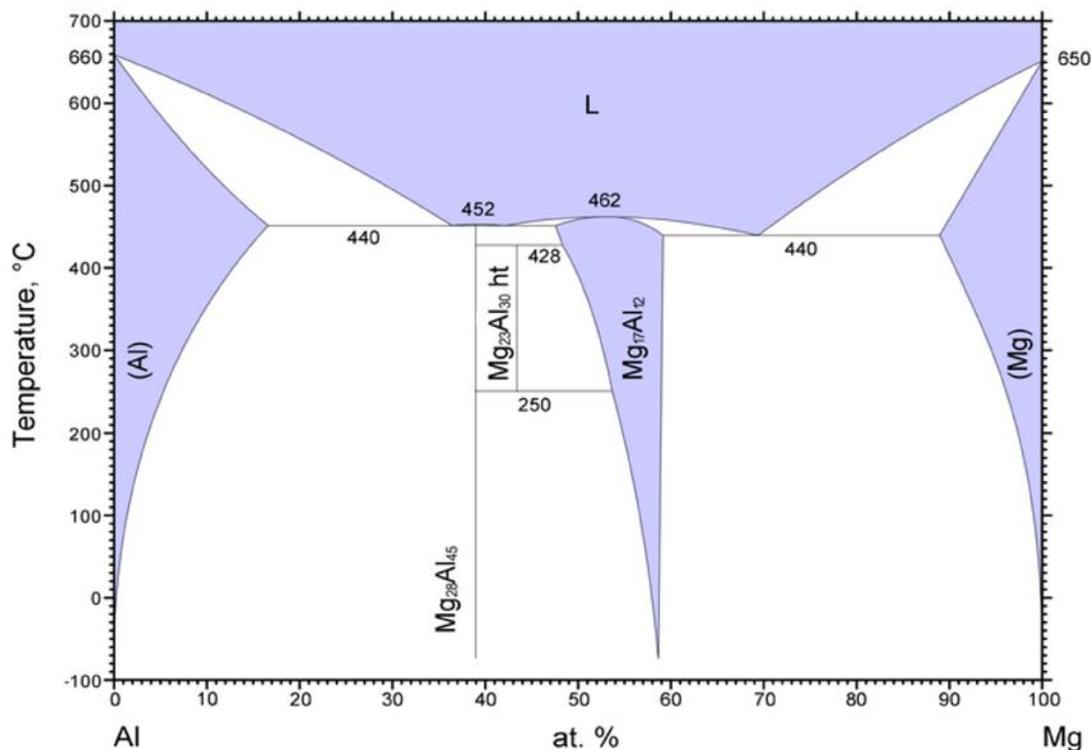
The liquidus is at 640 C for 2at%Al in Mg. As we cool from melt, solidificiation will begin at this temperature with composition k c_0= 0.72 at% Al. As we continue to cool, the liquid enriches in solute. The solid which forms is the solid in equilibrium with the liquid, therefore, the composition of the solid gradually increases in composition until we cool to the eutectic temperature, 440 C, where the liquid is at 30.7% Al and the solid is 11.1% Al. The phase fraction of liquid at this point is found using the non-equilibrium

lever rule:

$c_s = k\, c_0\, (1 - f_s)^{k-1}$
solve for f_l:
$[c_s/(k\, c_0)]^{1/(k-1)} = 1 - f_s = f_l$

$(0.111\, /\, (0.362 \times 0.02))^{1/(0.362-1)}$

0.0138585

Only the last 1.39% of the casting will have eutectic composition and microstructure. 98.61% of the casting by volume will be single phase.

The fraction of liquid when the solid composition is equal to c_0 is:

$(0.02\, /\, (0.362 \times 0.02))^{1/(0.362-1)}$

0.203386

Using this information, we can draw a curve of the composition as a function of position (where position is normalized to the total width of the casting, and the vertical axis is at% Al)
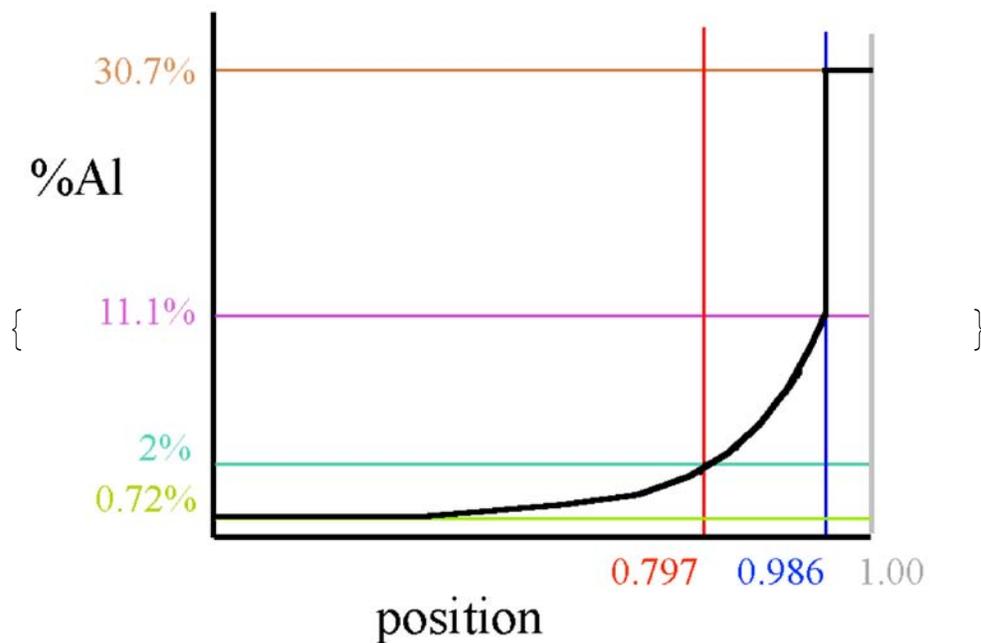
Problem 6

solute rejected from the solid = solute incorporated into the liquid
$df_s\, (C_l - C_s{}^{*}) = L\, dC_l$

Problem 7

B.C.: at x=0, then $f_s = 0$, and $C_l = C_0$ or equivalently $C_s{}^* = K C_0$.

Solve:
$df_s/L = dC_l/(C_l - C_s{}^*)$
substitute in $C_s{}^* = K\ C_l$:
$df_s/L = dC_l/(C_l - K\ C_l)$

integrate:
$f_s/L + A = \ln(C_l)/(1\text{-}K)$
exponentiate:
$\exp[(f_s/L + A)(1\text{-}K)] = C_l$
Factor out the integration constant, re-name it:
$C_l = B\exp[(1 - K)\ f_s/L)]$

apply B.C.:
$C_0 = B\exp[(1 - K)\ 0/L]$
$\therefore\ C_0 = B.$

$C_l = C_0\exp[(1 - K)\ f_s/L)] = C_s{}^*/K$

$$\boxed{C_s{}^* = KC_0\exp[(1 - K)\ f_s/L]}$$

Plots of $C_s{}^*$ vs. f_s:

```
Show[Plot[{0.01 e^{0.99 fs}, 0.1 e^{0.9 fs}, 0.2 e^{0.8 fs}, 0.5 e^{0.5 fs}, 0.9 e^{0.1 fs}}, {fs, 0, 1},
  AxesLabel → {Style["f_s", FontSize → 20], Style["C_s*/C_0", FontSize → 20]},
  PlotStyle → {Red, Orange, Green, Blue, Purple}],
 Graphics[{Text[Style["K=0.01", FontSize → 18, FontColor → Red], {0.9, 0.1}],
    Text[Style["K=0.1", FontSize → 18, FontColor → Orange], {0.9, 0.3}],
    Text[Style["K=0.2", FontSize → 18, FontColor → Green], {0.9, 0.5}],
    Text[Style["K=0.5", FontSize → 18, FontColor → Blue], {0.9, 0.7}],
    Text[Style["K=0.9", FontSize → 18, FontColor → Purple], {0.9, 0.9}]}]]
```
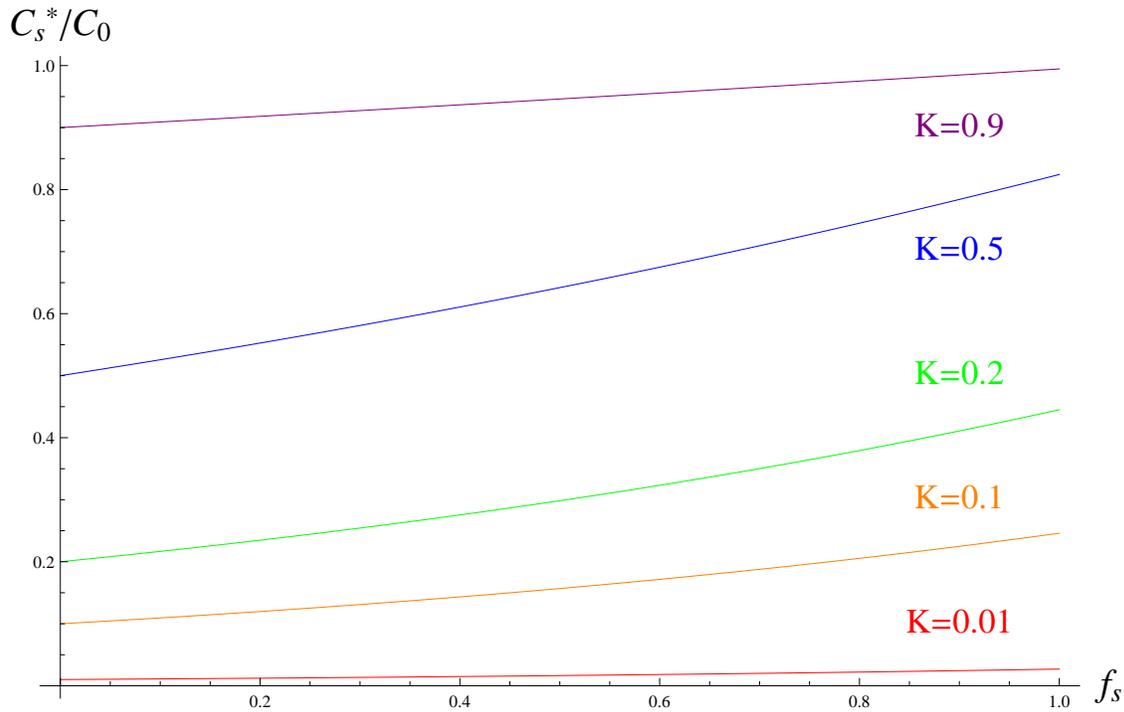

Problem 8

Elements with low K will be easiest to remove. The smaller K is, the more the solute is rejected from the solid. Therefore, Y is easiest to remove, followed by Zn, then Al. It would be very difficult to remove Li. Also, a smaller C_0 makes it easier to remove a given element. Y has the lowest solubility in Mg, so it will probably have a low C_0 too, followed by Zn, then Al.

3.044 Materials Processing

Spring 2013