

THERMODYNAMICS

1. A sheet of manganese (2 moles) at room temperature (298 K) is placed in thermal contact with a heat supply that slowly transfers 100,698 J of heat into the sample at constant pressure. Use the following thermodynamic data for Mn to answer the questions below:

Mn has four solid phases, α , β , γ , and δ :

$$\bar{C}_p^\alpha = 21.6 + 15.9 \times 10^{-3} T \frac{J}{K \cdot mole}$$

$$T_{trans}^{\alpha \rightarrow \beta} = 993K$$

$$\Delta \bar{H}_{trans}^{\alpha \rightarrow \beta} = 2,010 \frac{J}{mole}$$

$$\bar{C}_p^\beta = 34.9 + 2.8 \times 10^{-3} T \frac{J}{K \cdot mole}$$

$$T_{trans}^{\beta \rightarrow \gamma} = 1373K$$

$$\Delta \bar{H}_{trans}^{\beta \rightarrow \gamma} = 2,300 \frac{J}{mole}$$

$$\bar{C}_p^\gamma = 44.8 \frac{J}{K \cdot mole}$$

$$T_{trans}^{\gamma \rightarrow \delta} = 1409K$$

$$\Delta \bar{H}_{trans}^{\gamma \rightarrow \delta} = 1,800 \frac{J}{mole}$$

$$\bar{C}_p^\delta = 47.3 \frac{J}{K \cdot mole}$$

- Calculate the final temperature of the sample.
 - Calculate the total enthalpy change for this process.
 - Calculate the total entropy change for this process.
 - What phase (or phases) are present at equilibrium at the end of this process?
- a. Calculation of the final temperature is made by using the heat capacity data to determine how much heat is required to heat up and through the several phase transitions present. The calculation is readily carried out by simply determining how much heat is needed for heating to each phase transition:

Starting out at 298 K, we first heat the sample (α phase at room temperature) to the first phase transition $\alpha \rightarrow \beta$, at 993K:

$$q_{298K \rightarrow 993K} = \int_{298}^{993} n \bar{C}_p dT = \int_{298}^{993} (2 \text{ moles}) (21.6 + 15.9 \times 10^{-3} T \frac{J}{mole \cdot K}) dT = 44,290J$$

...clearly, we have more heat to use, so we continue. The phase transition consumes a small amount of heat:

$$q_{298K \rightarrow 993K} = n\Delta\bar{H}_{\alpha \rightarrow \beta} = (2)(2,010) = 4,020J$$

We continue summing up the heat for the next few transitions in a similar manner:

$$q_{993K \rightarrow 1373K} = \int_{993}^{1373} n\bar{C}_p^\beta dT = \int_{993}^{1373} (2 \text{ moles}) \left(34.9 + 0.0028T \frac{J}{\text{mole} \cdot K} \right) dT = 29,041J$$

$$q_{\beta \rightarrow \gamma} = n\Delta\bar{H}_{\beta \rightarrow \gamma} = (2)(2,300) = 4,600J$$

Our running total for heat transferred to reach the gamma phase at 1373K is now 81,951 J. This leaves 18,747 J of heat yet to be consumed. Continuing on to the next transition:

$$q_{1373K \rightarrow 2300K} = \int_{1373}^{1409} n\bar{C}_p^\gamma dT = \int_{1373}^{1409} (2 \text{ moles}) \left(44.8 \frac{J}{\text{mole} \cdot K} \right) dT = 3,226J$$

$$q_{\gamma \rightarrow \delta} = n\Delta\bar{H}_{\gamma \rightarrow \delta} = (2)(1,800) = 3,600J$$

We have 11,701 J of heat yet to use up. We determine the final temperature by integrating to use up the 'left over' heat in the delta phase:

$$q_{1409K \rightarrow T_f} = \int_{1409}^{T_f} n\bar{C}_p^\delta dT = \int_{1409}^{T_f} (2 \text{ moles}) \left(47.3 \frac{J}{\text{mole} \cdot K} \right) dT = 11,701J$$

$$94.6T_f - 133,291J = 11,701J$$

$$\therefore T_f = 1535K$$

b. Because this process occurs at constant pressure, we immediately know:

$$C_p = \left(\frac{dq_{rev}}{dT} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$dq_{rev} = dH$$

$$q_{rev} = \Delta H$$

$$\therefore \Delta H = 100,698J$$

c. We determine the total entropy change in a manner similar to the integrating procedure used in part (a):

First, the appropriate relation to get us started is:

$$C_p = \left(\frac{dq_{rev}}{dT} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

$$dS = \frac{C_p}{T} dT$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT$$

Note that the last equality and integral hold only for regions where no phase transition occurs. Using this expression, we integrate over the temperature change that occurs when the 100,698 J of heat are absorbed by the system:

$$\Delta S = \int_{298}^{993} \frac{n\bar{C}_p^\alpha}{T} dT + \frac{n\Delta H_{\alpha \rightarrow \beta}}{993K} + \int_{993}^{1373} \frac{n\bar{C}_p^\beta}{T} dT + \frac{n\Delta H_{\beta \rightarrow \gamma}}{1373K} + \int_{1373}^{1409} \frac{n\bar{C}_p^\gamma}{T} dT + \frac{n\Delta H_{\gamma \rightarrow \delta}}{1409K} + \int_{1409}^{1533} \frac{n\bar{C}_p^\delta}{T} dT$$

We account for the entropy of transition for each phase transformation crossed in the process with the terms containing the enthalpy and temperatures of transition. Plugging in and carrying out the integrations:

$$\Delta S = 119.1 \frac{J}{K}$$

- d. Our calculation in part (a) tells us that the delta phase is the final equilibrium structure of the system.

2. Twenty kg of liquid bismuth at 600 K is introduced into a 10 kg alumina (Al_2O_3) crucible (initial temperature 298K), filling the crucible to the top; the crucible and bismuth are then surrounded by adiabatic walls (illustrated below). At equilibrium, according to the zeroth law, the temperatures of the bismuth and alumina crucible must be equal. Use the following thermodynamic data to answer the questions below:

$$\bar{C}_p^{alumina, solid} = 106.6 + 0.0178T \frac{J}{K \cdot mole}$$

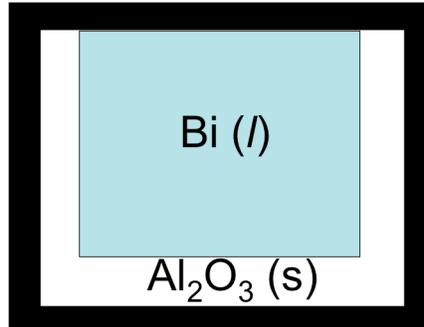
$$T_m^{alumina} = 2327K$$

$$\bar{C}_p^{Bi, solid} = 18.8 + 0.023T \frac{J}{K \cdot mole}$$

$$T_m^{Bi} = 544K$$

$$\bar{C}_p^{Bi, liquid} = 20 + 0.00615T \frac{J}{K \cdot mole}$$

$$\Delta \bar{H}_m^{Bi} = 10,900 \frac{J}{mole}$$



- What is the final temperature of the system?
- How much heat is transferred to the alumina?
- At the final equilibrium, is the bismuth liquid or solid?
- Consider now the same process, except that the adiabatic walls are removed. The closed system (can exchange heat...) of the bismuth in the alumina container is placed in a large room at $T = 298$ K, which behaves as a heat reservoir- it can transfer heat out of the system (or into it, depending on the temperatures of the reservoir and the system). At equilibrium, the bismuth and alumina will reach a final temperature of 298 K to match the environment of the room. How much heat will leave the bismuth to reach equilibrium?

- Because the crucible and liquid bismuth are enclosed by adiabatic walls, they can only exchange heat with one another. In other words, whatever heat leaves the bismuth must enter the alumina. This can be stated mathematically:

$$q_{Bi} = -q_{Al_2O_3}$$

The minus sign tells us that the direction of heat flow in the alumina is opposite that of the bismuth (e.g., heat flowing **out** of the bismuth is flowing **into** the alumina.) This equality immediately tells us how to determine the final temperature of the system- since it must be the same in the bismuth and the alumina:

$$q_{Bi} = -q_{Al_2O_3}$$

$$\int_{600}^{544} n_{Bi} \bar{C}_p^{Bi,l} dT - n_{Bi} \Delta \bar{H}_m + \int_{544}^{T_f} n_{Bi} \bar{C}_p^{Bi,s} dT = - \left[\int_{298}^{T_f} n_{Al_2O_3} \bar{C}_p^{Al_2O_3,s} dT \right]$$

A few comments: In writing the left-hand expression, we are making the assumption that the Bi will cool enough to pass through the melting point and solidify. Note that because we are passing from high to low temperature, we have a minus sign in front of the enthalpy of melting- we must remove heat from the sample to freeze it. To proceed, we need to calculate the number of moles of alumina and bismuth we have:

$$\text{Bi} : (20,000\text{g}) \left(\frac{\text{mole}}{208.9\text{g}} \right) = 95.7 \text{ moles}$$

$$\text{Al}_2\text{O}_3 : (10,000\text{g}) \left(\frac{\text{mole}}{101.96\text{g}} \right) = 98.08 \text{ moles}$$

Plugging in the given data for alumina and bismuth, we can calculate the final temperature of the system:

$$1.1T_f^2 + 1799T_f - 2,473,602 = -.8729T_f^2 + 3,193,206 - 10,455T_f$$

The expression reduces to a quadratic equation, which we can solve for T_f :

$$T_f = \frac{-12,254 \pm \sqrt{(12,254)^2 - 4(1.97)(-5,666,808)}}{2(1.93)} = 433\text{K}$$

- b. The heat transferred to the alumina is just one side of the heat equality expression above:

$$1.1T_f^2 + 1799T_f - 2,473,602 = -q_{\text{Al}_2\text{O}_3}$$

$$q_{\text{Al}_2\text{O}_3} = 1,488,397\text{J}$$

- c. The final temperature falls well below the melting point of Bi, so the sample has solidified.
 d. We simply calculate the heat transfer that occurs to move Bi from liquid at 600K to solid Bi at 298K:

$$q_{\text{Bi}} = \int_{600}^{544} n_{\text{Bi}} \bar{C}_p^{\text{Bi},l} dT - n_{\text{Bi}} \Delta \bar{H}_m + \int_{544}^{298} n_{\text{Bi}} \bar{C}_p^{\text{Bi},s} dT = -1,839\text{kJ}$$

3. Magnetic resonance imaging (MRI) is a common medical technique used for diagnostic imaging of tissues in patients. MRI is based on measuring the response of the weak magnetic dipoles in the atoms of tissues under a strong applied magnetic field. Typically, the magnetic induction in a clinical MRI machine may be ~2 Tesla. Consider the materials used to fabricate the MRI chamber that will be placed in the magnetic field, such as aluminum.
- What magnetic field strength is required to achieve a 2T induction in the MRI housing if the housing is fabricated from aluminum?
 - Will the magnetization induced in the aluminum be significant compared to, say, an iron permanent magnet that has a maximal net magnetization of $1.39 \times 10^5 \text{ A/m}$? Support your answer with a calculation.
 - What is the work performed by the magnetic field in the volume of a section of the MRI aluminum housing 1 m x 1 m and 5 mm thick?

a. We use the expression relating field strength **H** to induction **B**:

$$B = 2T = \mu_o H + \mu_o M = \mu_o(1 + \chi)H$$

From the class notes, we have the susceptibility for Al:

$$\chi = 2.07 \times 10^{-5}$$

$$B = 2T = 2 \frac{kg}{s \cdot C} = \left(4\pi \times 10^{-7} \frac{kg \cdot m}{C^2} \right) (1 + 2.07 \times 10^{-5}) H$$

$$\therefore H = 1.59 \times 10^6 \frac{C}{m \cdot s} = 1.59 \times 10^6 \frac{A}{m}$$

b. The magnetization is calculated directly:

$$M = \chi H = 32.9 \frac{A}{m}$$

...this is only 0.02% of the magnetization of the example iron permanent magnet!

c. The work is:

$$w = \int_0^{1.59 \times 10^6} V \mu H dH = V \mu_o (1 + \chi) \frac{H^2}{2} \Big|_0^{1.59 \times 10^6} = 7,942 J$$

Problem Set 2 - Bonding

1. Recall: an operator \hat{O} is linear if $\hat{O}(\alpha_1 f_1 + \alpha_2 f_2) = \alpha_1 \hat{O}(f_1) + \alpha_2 \hat{O}(f_2)$
(where f_1, f_2 are two functions and α_1, α_2 are two constants)

(a) It can be verified that $\hat{O}(\alpha_1 f_1(x) + \alpha_2 f_2(x)) = \frac{d^2}{dx^2} \{ \alpha_1 f_1(x) + \alpha_2 f_2(x) \} = \alpha_1 \frac{d^2}{dx^2} f_1(x) + \alpha_2 \frac{d^2}{dx^2} f_2(x) = \alpha_1 \hat{O}(f_1(x)) + \alpha_2 \hat{O}(f_2(x))$. Thus, the operator \hat{O} is linear.

(b) For this operator $\hat{O}(\alpha_1 f_1(x) + \alpha_2 f_2(x)) = \left(\frac{d}{dx} \{ \alpha_1 f_1(x) + \alpha_2 f_2(x) \} \right)^2 = \alpha_1^2 \left(\frac{df_1(x)}{dx} \right)^2 + 2\alpha_1 \alpha_2 \frac{df_1(x)}{dx} \frac{df_2(x)}{dx} + \alpha_2^2 \left(\frac{df_2(x)}{dx} \right)^2 \neq \alpha_1 \hat{O}(f_1(x)) + \alpha_2 \hat{O}(f_2(x))$. Thus, \hat{O} is not linear.

2. Recall: commutator between \hat{A} and $\hat{B} = [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

(a) $[\hat{x}, \hat{p}_x] \psi(x) = [x, -i\hbar \frac{d}{dx}] \psi(x) = x \left(-i\hbar \frac{d}{dx} \psi(x) \right) - (-i\hbar \frac{d}{dx} (x\psi(x)))$
 $= -i\hbar \left(x \frac{d}{dx} \psi(x) - \psi(x) - x \frac{d}{dx} \psi(x) \right) = i\hbar \psi(x)$.

Thus, the commutator reduces to a multiplicative constant: $[\hat{x}, \hat{p}_x] = i\hbar$
(\hat{x} and \hat{p}_x do not commute).

(b) This time, since the operators involve both x and y , we need to consider a wavefunction of the form $\psi(x, y)$.

$[\hat{x}, \hat{p}_y] \psi(x, y) = [x, -i\hbar \frac{\partial}{\partial y}] \psi(x, y) = x \left(-i\hbar \frac{\partial}{\partial y} \psi(x, y) \right) - (-i\hbar \frac{\partial}{\partial y} (x\psi(x, y)))$
 $= -i\hbar \left(x \frac{\partial}{\partial y} \psi(x, y) - x \frac{\partial}{\partial y} \psi(x, y) \right) = 0$

Consequently, the commutator is zero: $[\hat{x}, \hat{p}_y] = 0$ (\hat{x} and \hat{p}_y commute).

3. (a) The potential felt by an electron in the presence of the nucleus of a helium atom ($Z = 2$) can be written as:

$$V(r) = \frac{\text{charge(nucleus)} \times \text{charge(electron)}}{4\pi\epsilon_0 r} = -(Ze^2)/(4\pi\epsilon_0 r) = -(2e^2)/(4\pi\epsilon_0 r)$$

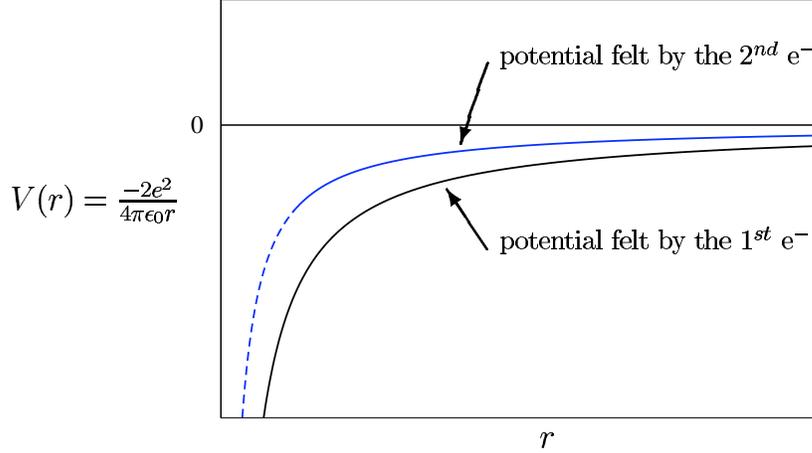
(see figure on next page)

(b) He^+ is an hydrogen-like ion (hydrogenoid atom with $Z = 2$). The energy levels are thus given by $E_n = (-13.6058 \text{ eV}) \frac{Z^2}{n^2} = -\frac{54.4232}{n^2} \text{ eV}$.

(cf. lecture 5 "Three Quantum Numbers")

(c) From far away, the He^+ ion can be seen as a single positive charge (cf. Gauss theorem). The potential can be assimilated to that of a hydrogen nucleus.

$V_{\text{second electron}}(r) \approx -(e^2)/(4\pi\epsilon_0 r)$ when r is large.



4. i) The volume \mathcal{V} of a spatial region Ω is given by $\mathcal{V} = \int_{\Omega} d\vec{r}$.
 ii) A shell of outer radius R and thickness h can be defined as the spatial region $\Omega : \begin{cases} R-h < r < R \\ 0 < \theta < \pi \\ 0 < \phi < 2\pi \end{cases}$
 iii) integrals in spherical coordinates: $\int f(\vec{r}) d\vec{r} = \int_r \int_{\theta} \int_{\phi} f(r, \theta, \phi) r^2 \sin(\theta) dr d\theta d\phi$

As a result, the volume \mathcal{V} of the skin of a Valencia orange of thickness $h = 0.005$ m and outer radius $R = 0.05$ m is:

$$\begin{aligned}
 \mathcal{V} &= \int_{r=R-h}^{r=R} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} r^2 \sin(\theta) dr d\theta d\phi \\
 &= \left(\int_{R-h}^R r^2 dr \right) \times \left(\int_0^{\pi} \sin(\theta) d\theta \right) \times \left(\int_0^{2\pi} d\phi \right) \\
 &= \left(\int_{R-h}^R r^2 dr \right) \times 2 \times 2\pi
 \end{aligned} \tag{1}$$

As expected, $\mathcal{V} = \frac{4\pi}{3}(R)^3 - \frac{4\pi}{3}(R-h)^3 = 1.42 \times 10^{-4} \text{ m}^3$.

5. i) classical quantity: $V(r) = -e^2/(4\pi\epsilon_0 r)$
 ii) correspondence principle: $r \rightarrow r$
 iii) quantum operator: $\widehat{V}(r) = V(r) = -e^2/(4\pi\epsilon_0 r)$
 iv) expectation value (note that $\psi_{2s}(r) = \psi_{n=2, l=0, m=0}(r) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$

is already normalized):

$$\begin{aligned}\langle V(r) \rangle &= \int_{r=0}^{r=+\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \psi_{2s}^*(r) \{V(r)\psi_{2s}(r)\} r^2 \sin(\theta) dr d\theta d\phi \\ \langle V(r) \rangle &= 4\pi \int_{r=0}^{r=+\infty} V(r) \psi_{2s}^*(r) \psi_{2s}(r) r^2 dr \\ \langle V(r) \rangle &= -\frac{e^2}{\epsilon_0} \int_{r=0}^{r=+\infty} \left\{ \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \right\}^2 r dr \\ \langle V(r) \rangle &= -\frac{e^2}{32\pi\epsilon_0 a_0^3} \int_0^{+\infty} r \left(2 - \frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}} dr\end{aligned}$$

Using mathematica or maple ¹, we obtain: $\langle V(r) \rangle = -e^2/(16\pi\epsilon_0 a_0) = -1/2 \text{ Ryd}$.

The expectation value for the potential energy is thus twice the total energy:

$$\underline{E_{n=2} = \langle \frac{\hat{p}^2}{2m} + V(r) \rangle = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{1}{2^2} = -1/4 \text{ Ryd}}$$

To calculate the expectation value for the kinetic energy, we can use the fact that $\langle \frac{\hat{p}^2}{2m} + V(r) \rangle = \langle \frac{\hat{p}^2}{2m} \rangle + \langle V(r) \rangle$. Hence $\underline{\langle \frac{\hat{p}^2}{2m} \rangle = -1/4 + 1/2 \text{ Ryd} = 1/4 \text{ Ryd}}$.

6. The orthogonality condition between $\psi_{1s}(r)$ and $\psi_{2s}(r)$ can be written as:

$$\langle \psi_{1s} | \psi_{2s} \rangle = \int_{space} \psi_{1s}^*(r) \psi_{2s}(r) d\vec{r} = 0 \text{ (note that there is no arrow on } r \text{)}$$

In spherical coordinates, this condition can be rewritten as:

$$4\pi \int_0^{+\infty} \psi_{1s}^*(r) \psi_{2s}(r) r^2 dr = 0, \text{ or } \int_0^{+\infty} r^2 e^{-\frac{r}{a_0}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} dr = 0$$

Again, using mathematica or maple ², it can be verified that $\underline{\langle \psi_{1s} | \psi_{2s} \rangle = 0}$.

7. From the graphs (next page), it can be seen that:

- d_{z^2} has 2 conical nodal surfaces; d_{xz} , d_{yz} have 1 vertical nodal plane and 1 horizontal nodal plane; $d_{x^2-y^2}$, d_{xy} have 2 vertical nodal planes;

- $R_{n=3, l=2}(r)$ has no node.

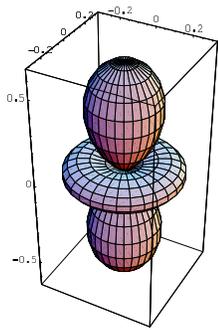
8. When the angular momentum quantum number is $l = 1$, the possible values of the magnetic quantum number are $\underline{m = -1, 0, +1}$ (recall: $m = -l, -l + 1, l - 1, l$).

From the graph of $R_{n=3, l=1}(r) = R_{3p}(r)$ (Engel, Reid Figure 20.6 p 444), there is 1 radial node (note that the node at the origin is never taken into account).

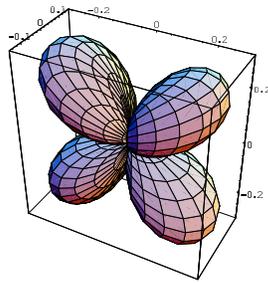
More generally, the number of nodes in the radial wavefunction R_{nl} is $n - l - 1$.

¹If you like sport, you can also prove that $\int_0^{+\infty} r^n e^{-\frac{r}{\alpha a_0}} dr = n \times (n-1) \times \dots \times 2 \times 1 \times (\alpha a_0)^{n+1}$ (integration by parts); and use this equality to calculate the expectation value: $\langle V(r) \rangle = -\frac{e^2}{32\pi\epsilon_0 a_0^3} (4 - 8 + 6) a_0^2$.

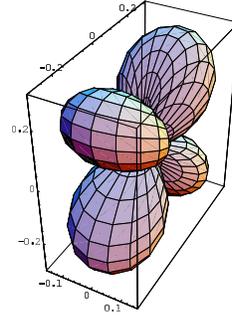
²By hand, using the previous formula, $\int_0^{+\infty} r^2 e^{-\frac{r}{a_0}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} dr = a_0^3 (2 \times 2 \times (2/3)^3 - 3 \times 2 \times (2/3)^4)$.



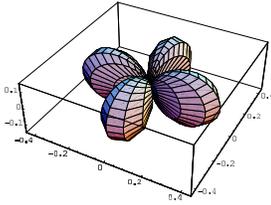
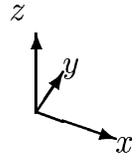
(a) $d_{z^2} = Y_{l=2,m=0}$



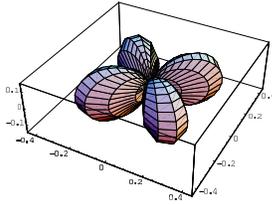
(b) $d_{xz} \propto \text{Re}(Y_{l=2,m=1})$



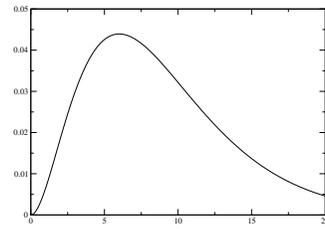
(c) $d_{yz} \propto \text{Im}(Y_{l=2,m=1})$



(d) $d_{x^2-y^2} \propto \text{Re}(Y_{l=2,m=2})$



(e) $d_{xy} \propto \text{Im}(Y_{l=2,m=2})$



(f) $a_0^{3/2} \times R_{n=3,l=2}(r)$