

Problem Set 3 - Bonding

1. i) energy of a photon $E(\text{photon}) = h\nu(\text{photon})$
ii) frequency-wavelength relation: $c = \lambda(\text{photon})\nu(\text{photon})$
Thus, $\lambda(\text{photon}) = hc/E(\text{photon}) = 1240 \text{ nm}$.

2. Cf. Lecture 1bis (“Principle of Linear Superposition”, “Wave-particle Duality”, Electron Diffraction/Double-Slit Experiment)
Engel, Reid: Section 12.6

3. wavefunction of the free electron in 3D: $\Psi(\vec{r}, t) = Ae^{i\vec{k}\vec{r} - i\omega t} = Ae^{i(k_x x + k_y y + k_z z - \omega t)}$.
Cf Lecture 1bis (“A travelling Plane Wave”)

You can check that:

- i) $-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r}, t) = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\}\Psi(\vec{r}, t) = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)\Psi(\vec{r}, t)$
ii) $i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t) = \hbar\omega\Psi(\vec{r}, t)$

As a consequence, the wavefunction $\Psi(\vec{r}, t) = Ae^{i(k_x x + k_y y + k_z z - \omega t)}$ verifies the SSE under the condition that $E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$.

The TDSE is satisfied provided that $\hbar\omega = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$ (Cf recitation 1 problem II (a5) for further details).

4. i) kinetic energy of the electron $E_k(\text{electron}) = p(\text{electron})^2/2m(\text{electron})$
Thus, $p(\text{electron}) = \sqrt{2m(\text{electron})E_k(\text{electron})} = 5.40 \times 10^{-25} \text{ kg.m.s}^{-1}$.

- ii) de Broglie relation $\lambda(\text{electron})p(\text{electron}) = h$
Consequently, $\lambda(\text{electron}) = h/p(\text{electron}) = 1.22 \text{ nm}$

5. For a time-independent potential, making the *ansatz* $\Psi(\vec{r}, t) = \psi(\vec{r})f(t)$ (separation of variables) in the TDSE, one obtains:

$$-\frac{\hbar^2}{2m}f(t)\nabla^2\psi(\vec{r}) + V(\vec{r})f(t)\psi(\vec{r}) = i\hbar\psi(\vec{r})\frac{\partial}{\partial t}f(t).$$

Dividing by $\psi(\vec{r})f(t)$:

$$\frac{1}{\psi(\vec{r})}\left\{-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r})\right\} = i\hbar\frac{1}{f(t)}\frac{\partial}{\partial t}f(t).$$

A t -dependent function cannot equal a \vec{r} -dependent function unless these functions are equal to the same constant E . Thus:

$$\frac{1}{\psi(\vec{r})}\left\{-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r})\right\} = E \text{ and } i\hbar\frac{1}{f(t)}\frac{\partial}{\partial t}f(t) = E$$

The first equation gives the SSE from which $\psi(\vec{r})$ can be determined. From the second equation ($i\hbar\frac{\partial}{\partial t}f(t) = Ef(t)$), the time-dependent part $f(t)$ can be calculated ($f(t) \propto$

$e^{-iEt/\hbar}$).

6. Cf. Engel, Reid: Section 15.3 (note that in our case the dimensions of the box are a in all spatial directions)

7. Keywords: quantum tunnelling, probing the exponential tail
Cf Lecture 4 (“Metal Surfaces”, “Scanning Tunnelling Microscopy”)
Engel, Reid: Section 16.6

8. Linear operator: an operator \hat{O} (acts on a wavefunction to give another wavefunction) 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)

9. Cf. Lecture 4 (“Fourth Postulate”)

10. Surface of the earth: $S(\text{earth}) = \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} R^2(\text{earth}) \sin(\theta) d\theta d\phi = R^2(\text{earth}) \times \int_{\theta=0}^{\theta=\pi} \sin(\theta) d\theta \times \int_{\phi=0}^{\phi=2\pi} d\phi = 4\pi R^2(\text{earth}) = 5.15 \times 10^{14} \text{ m}^2$.

11. Engel, Reid: Section 14.2

12. Since the potential is central ($V = V(r) = -e^2/(4\pi\epsilon_0 r)$), one can try to separate variables in the SSE: $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$.

The commutation between \hat{H} , \hat{L}^2 and \hat{L}_z tells us that $\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$, where $Y_{lm}(\theta, \phi)$ is a spherical harmonic.

Substituting in the SSE $\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$ (recall that $\hat{H} = -\frac{\hbar}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}$), we obtain the equation $-\frac{\hbar}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 R(r) + \frac{\hbar^2 l(l+1)}{2mr^2} R(r) - \frac{e^2}{4\pi\epsilon_0 r} R(r) = ER(r)$ (the first term corresponds to the radial kinetic energy, the second to the angular kinetic energy/centripetal contribution to the energy, and the third to the potential/Coulomb energy). This equation can be solved by making another *ansatz*: $R(r) = L(r)e^{\alpha r}$ (where $L(r)$ and unknown polynomial and α an unknown constant).

Cf. Questions/Answers (posted on the class web site → Study Materials)

Engel, Reid: Section 20.3

13. 4 quantum numbers:

n =principal quantum number, related to the total energy of an electron in the presence of an atomic nucleus.

l =angular momentum quantum number, related to the square of the angular momentum

m =magnetic quantum number, related to the projection of the angular momentum on a given axis (often the z -axis)

s =spin quantum number, related to the spin of the electron (Cf. Stern-Gerlach experiment)

Cf. Lecture 5, Cf. Lecture 7 (“Spin Eigenvalues/Eigenvalues”)

14. As seen in Problem Set 2, the expectation for the potential energy for an electron in the hydrogen atom is twice the total energy: $\langle V(r) \rangle = 2 \times \left(-\frac{1}{n^2}\right) = -1/2$ Ryd

15. The He atom because of electron-electron screening.

Cf. Lecture 8

Engel, Reid: Section 21.1

16. Cf. Lecture 9

THERMODYNAMICS

1. **Why is it hard to make measurements at constant volume?** We have discussed in class that experimentally, C_v is difficult to measure due to thermal expansion. Let's quantify this difficulty: Suppose you have 1 mole of iron that has a volume of 7.31 cm^3 at 293 K. Determine the pressure that would have to be applied after this material is heated to 298 K (only 5 degrees warmer!) to compress it to the volume it had at 293K- thus maintaining constant volume.

Data for Fe: $\alpha = 6.3 \times 10^{-5} \text{ K}^{-1}$
 $\kappa = 1.10 \times 10^{-6} \text{ atm}^{-1}$ at 298K

We start with the formula for the thermal expansion coefficient, in order to calculate the amount of expansion that occurs when the temperature is raised to 298K:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$\alpha dT = \frac{dV}{V}$$

$$\int_{T_L}^{T_H} \alpha dT = \int_{V_L}^{V_H} \frac{dV}{V}$$

$$\alpha(T_H - T_L) = \alpha \Delta T = \ln \frac{V_H}{V_L}$$

Thus the volume after heating is:

$$V_H = V_L e^{\alpha \Delta T}$$

Next, we need to determine the pressure required to compress the material back to V_L :

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$dP = -\frac{1}{\kappa V} dV$$

$$\Delta P = -\frac{1}{\kappa} \int_{V_H}^{V_L} \frac{dV}{V} = \frac{1}{\kappa} \ln \frac{V_H}{V_L} = \frac{1}{\kappa} \ln \frac{V_L e^{\alpha \Delta T}}{V_L} = \frac{\alpha \Delta T}{\kappa} = 286.3 \text{ atm}$$

...thus the difficulty in making constant volume measurements. Even this small re-compression requires quite a significant applied pressure.

2. **Thermal properties of gases.** Calculate the thermal expansion coefficient and isothermal compressibility of an ideal gas.

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$V = \frac{nRT}{P}$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}$$

$$\alpha = \frac{1}{V} \left(\frac{nR}{P} \right) = \left(\frac{P}{nRT} \right) \left(\frac{nR}{P} \right) = \frac{1}{T}$$

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$V = \frac{nRT}{P}$$

$$\left(\frac{\partial V}{\partial P} \right)_T = -\frac{nRT}{P^2}$$

$$\therefore \kappa = -\frac{1}{V} \left(-\frac{nRT}{P^2} \right) = \left(\frac{P}{nRT} \right) \left(\frac{nRT}{P^2} \right) = \frac{1}{P}$$

3. **Cooking with a sealed pot.** Engel and Reid problem P3.5, p. 59.

We make use of the expression derived in class relating temperature/volume changes to pressure changes in a material:

$$dP = \frac{\alpha}{\kappa} dT - \frac{1}{V\kappa} dV$$

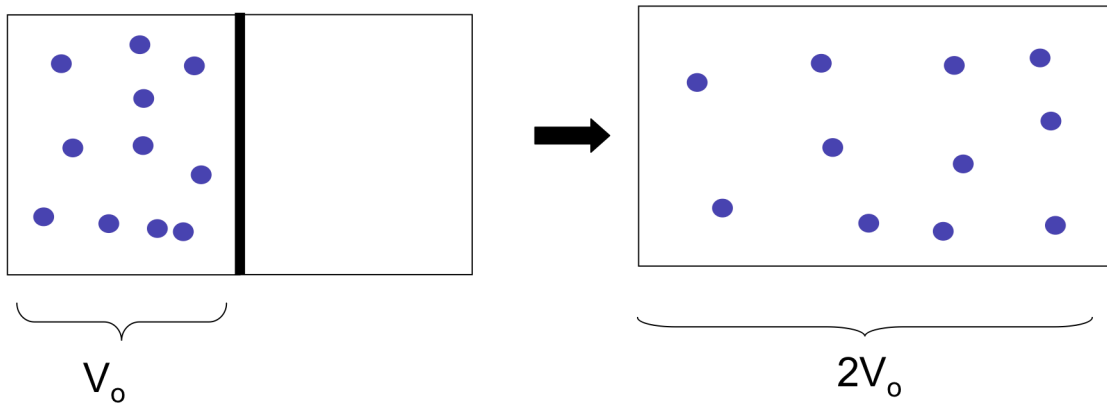
Taking the α and κ as approximately constant during this process, we can integrate the first term directly:

$$\int_{298}^{333} \frac{\alpha}{\kappa} dT = \left(\frac{2.04 \times 10^{-4} K^{-1}}{4.59 \times 10^{-5} bar^{-1}} \right) (333K - 298K) = 156 bar$$

To integrate the second term, we need to estimate the volume change allowed during the expansion. Since the thermal expansion coefficient of the vessel is smaller than that of water, the expansion of the vessel will be the limiting factor. We can calculate the volume change allowed by the vessel:

$$\alpha_{\text{vessel}} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

4. **Irreversibility of a free expansion.** Recall in lecture 2 that we discussed irreversible processes, and gave several examples- one of these example irreversible processes was the expansion of a gas to fill a vacuum. All irreversible processes only occur in one direction spontaneously because it is in this direction that the entropy of the universe is increased, in accord with the second law. Let's show this for the irreversible expansion: consider the diagram below. An ideal gas is initially contained in one half of a chamber with adiabatic walls, the volume of the half of the chamber containing the gas is V_0 . The partition between the right and left halves is suddenly removed, and the gas expands isothermally and adiabatically to fill the entire space ($V_f = 2V_0$). Show that this process fulfills the requirements of the second law for spontaneity by calculating the entropy change in the gas, the surroundings, and the universe, and show that for the process to run in reverse (spontaneous collapse of the gas back to one half of the chamber) will violate the second law.



$$dS_{\text{universe}} = dS_{\text{system}} + dS_{\text{surr}} = dS_{\text{system}} = \frac{dU}{T} + \frac{P}{T} dV$$

Because the temperature is held constant and for an ideal gas $U = U(T)$, the internal energy is constant:

$$dS_{\text{universe}} = 0 + \left(\frac{nRT}{V} \right) \frac{dV}{T} = \frac{nR}{V} dV$$

$$\therefore \Delta S_{\text{universe}} = nR \ln \frac{V_f}{V_i} = nR \ln 2 > 0$$

Because the entropy change in the universe is positive, the process is spontaneous. For the process to run in reverse, the entropy change is negative:

$$\Delta S_{universe} = nR \ln \frac{V_f}{V_i} = nR \ln \frac{1}{2} = -nR \ln 2 < 0$$

5. Let's revisit the liquid bismuth adiabatic cooling problem we examined on the last problem set. The physical situation is described again below, and the physical data for the system is also given. From your calculations on the last problem set, you showed that the alumina crucible and bismuth equilibrate at a final temperature of 433 K. Demonstrate that this process (cooling of the bismuth, warming of the alumina crucible) obeys the second law of thermodynamics, by calculating the total entropy change of the universe for the process.

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) and the system is allowed to equilibrate. At equilibrium, according to the zeroth law, the temperatures of the bismuth and alumina crucible must be equal. Use the following thermodynamic data:

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

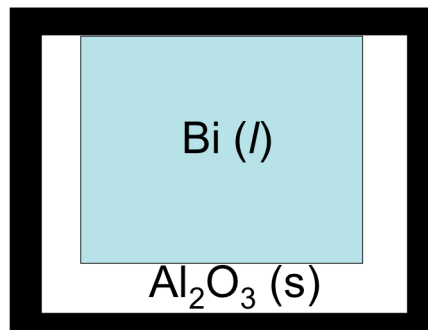
$$T_m^{alumina} = 2327K$$

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

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

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

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



To show the process is spontaneous, we must calculate the entropy change in the universe:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr} = \Delta S_{system} + 0$$

$$\Delta S_{universe} = \Delta S_{Bi} + \Delta S_{Al_2O_3}$$

We know the entropy change in the surrounding is zero because the only energy transfer occurring here is heat transfer, and the samples are surrounded by an adiabatic boundary- thus no heat is moving into the surroundings to change their entropy.

$$\Delta S_{Al_2O_3} = \int_{T_i}^{T_f} n \frac{\overline{C}_{Al_2O_3}^p}{T} dT = \int_{298}^{433} (98.08) \frac{(106.6 + 0.0178T)}{T} dT$$

$$\Delta S_{Al_2O_3} = 4.14 \frac{J}{K}$$

$$\Delta S_{Bi} = \int_{600}^{544} n \frac{\overline{C}_{Bi}^l}{T} dT - \frac{n\Delta\overline{H}_m}{T} + \int_{544}^{433} n \frac{\overline{C}_{Bi}^s}{T} dT = -2.79 \frac{J}{K}$$

$$\Delta S_{universe} = \Delta S_{Bi} + \Delta S_{Al_2O_3} = 1.35 \frac{J}{K}$$

Since the entropy change of the universe is positive, the process is predicted to be spontaneous.

6. **Confirming your intuition using the second law.** Using your ability to calculate entropy and enthalpy changes at phase transitions and the data given below for nickel, consider the following possible processes and confirm your intuition by a calculation showing whether the process is spontaneous or not according to the second law. The key to this problem is to correctly identify what heat is transferring between the system and the surroundings in these processes, and to carefully calculate the entropy changes for the system. Also critical: pay attention to the number of significant figures you carry in your calculation.

- One mole of solid nickel at 1716 K isothermally transforms completely to liquid at this temperature. The surroundings are a heat bath at 1716 K, and the process occurs at constant pressure.
- One mole of solid (superheated) nickel at 1736 K isothermally transforms completely to liquid at this temperature. The surroundings are a heat bath at 1736 K, and the process occurs at constant pressure.

$$\overline{C}_p^s = 16.49 + 0.0187T \frac{J}{K \cdot mole} \quad T_m = 1726K \quad \Delta\overline{H}_m = 17.47 \frac{kJ}{mole}$$

$$\overline{C}_p^l = 38.91 \frac{J}{K \cdot mole}$$

- The transformation we are concerned with is shown schematically below on qualitative plots of the entropy and enthalpy of the system near the temperature of interest. Our process is isothermal and isobaric. To test for spontaneity, we need, as in the above problems, to calculate the entropy change in the universe:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$$

The entropy change in the system will be given by the entropy change along the dashed line from A to B on the entropy plot below. We calculate the length of this line segment as illustrated graphically in the plot:

$$\Delta S_{system} = \Delta S_m - \Delta S_1 + \Delta S_2$$

$$\Delta S_m = \frac{\Delta H_m}{T_m} = 10.12 \frac{J}{K}$$

$$\Delta S_1 = \int_{1716}^{1726} n \frac{\bar{C}_p^l}{T} dT = \int_{1716}^{1726} (1) \frac{(38.91)}{T} dT = 38.91 \ln \frac{1726}{1716} = 0.226 \frac{J}{K}$$

$$\Delta S_2 = \int_{1716}^{1726} n \frac{\bar{C}_p^s}{T} dT = \int_{1716}^{1726} (1) \frac{(16.49 + 0.0187T)}{T} dT = 16.49 \ln \frac{1726}{1716} + 0.0187(1726 - 1716) = 0.0958 + 0.187 = 0.283 \frac{J}{K}$$

$$\therefore \Delta S_{system} = 10.18 \frac{J}{K}$$

Because the surroundings are at constant temperature, and we assume no work is occurring, the entropy change in the surroundings derives completely from the heat transfer from the system to the surroundings:

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H_{sys}}{(1716K)}$$

$$\Delta H_{sys} = \Delta H_m - \Delta H_1 + \Delta H_2 = 17,470 - 389.1 + 486.7 = 17.57 kJ$$

$$\Delta H_1 = \int_{1716}^{1726} n \bar{C}_p^l dT = \int_{1716}^{1726} (1)(38.91) dT = 389.1 J$$

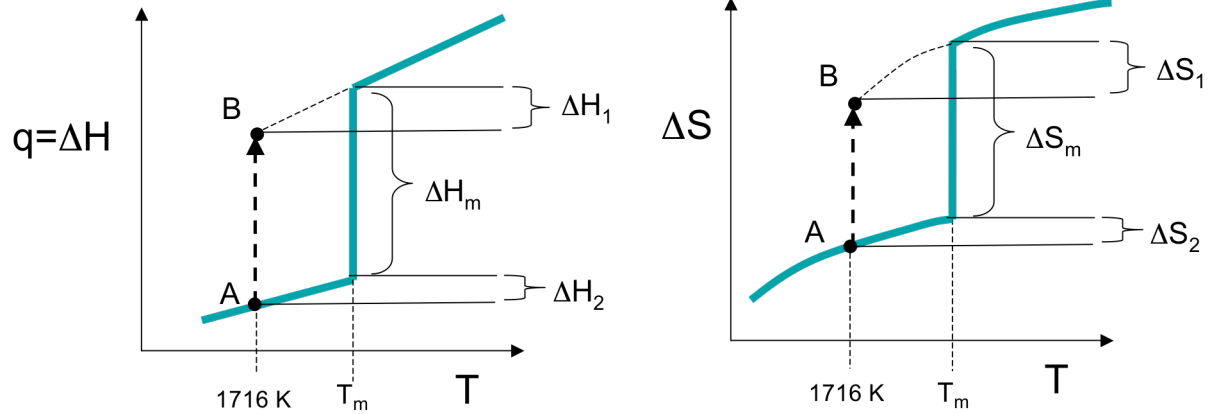
$$\Delta H_2 = \int_{1716}^{1726} n \bar{C}_p^s dT = 16.49(1726 - 1716) + \frac{0.0187}{2}(1726^2 - 1716^2) = 164.9 + 321.8 = 486.7 J$$

$$\therefore \Delta S_{surr} = -10.23 \frac{J}{K}$$

Finally, the total entropy change of the universe is:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr} = 10.18 - 10.23 = -0.05 \frac{J}{K}$$

Since the entropy change is less than zero, this process will not occur.



- b. Now, we follow the exact same scheme to predict the spontaneity of melting a superheated solid nickel sample: We must show that the entropy change of the universe in this process is positive:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$$

$$\Delta S_{system} = \Delta S_m - \int_{1726}^{1736} n \frac{\bar{C}_p^s}{T} dT + \int_{1726}^{1736} n \frac{\bar{C}_p^l}{T} dT = 10.12 - .282 + 0.225 = 10.06 \frac{J}{K}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{(1736K)} = \frac{-\Delta H_{sys}}{(1736K)}$$

$$q_{sys} = \Delta H_m - \int_{1726}^{1736} n \bar{C}_p^s dT + \int_{1726}^{1736} n \bar{C}_p^l dT = 17.37 kJ$$

$$\therefore \Delta S_{surr} = -10.01 \frac{J}{K}$$

$$\therefore \Delta S_{universe} = 0.05 \frac{J}{K}$$

...which is a spontaneous process.