Thermodynamics of Materials 3.00 Fall 2000

Solution for Problem Set 5

5.1 Problem statement Calculate the minimum number of joules per cubic meter required to heat a room of ideal monatomic gas from 10°C to 20°C at constant atmospheric pressure.

Solution

The minimum amount of heat needed is the amount of heat expended during reversible heating, dq_{rev}. The total amount of heat per unit volume is

$$\frac{dq_{rev}}{V} = \frac{n}{V}\overline{C}_p dT = \frac{P}{RT}\overline{C}_p dT$$

Using $\overline{C}_p = \frac{5}{2}R$ and integrating we get

$$\frac{\Delta q_{rev}}{V} = \frac{5}{2}P\int_{283K}^{293K}\frac{dT}{T} = \frac{5}{2}\cdot 1.01\times 10^5 \mathrm{Pa}\ln\frac{293K}{283K} = 8768 \text{ Pa}$$

5.2 Problem statement

Consider heating a body A, of constant heat capacity 1J/°C and initially at temperature 100K, to a final temperature of 200K. The heating takes place by sequentially placing it in thermal contact with N different large thermal reservoirs (so large that their temperature does not change during thermal contact).

On the same graph, plot the change in (1) entropy of the body A and (2) the change in entropy of the universe as a function of $1/N$.

Solution

In general, at constant pressure with constant C_p where A stands for the body A, u for the universe and r for the reservoir, T_0 is the initial temperature and T_f is the final temperature, the change in entropy of the body A is given by:

$$\Delta S_A = \int_{T_0}^{T_f}\frac{C_p}{T}dT = C_p\ln\frac{T_f}{T_0}$$

and the change in entropy of the universe by:

$$\Delta S_u = \Delta S_A + \Delta S_r = \Delta S_A + \frac{\Delta H_r}{T_r} = \Delta S_A - \frac{\Delta H_A}{T_r}$$

The change in entropy of the reservoir (surroundings) is given by the following integral:

$$\Delta S_r = -\frac{\int_{T_0}^{T_f} C_p dT}{T_r} = -C_p\frac{T_f - T_0}{T_f}$$

Let's examine the behaviour of these expressions for the processes in the homework problem. For N = 1: $\Delta S_A = C_p\ln\frac{200K}{100K} = C_p\ln 2$

For N = 2: $\Delta S_A = C_p\ln\frac{150K}{100K} + C_p\ln\frac{200K}{150K} = C_p\ln 2$

For N = 3: $\Delta S_A = C_p\ln\frac{133K}{100K} + C_p\ln\frac{166K}{133K} + C_p\ln\frac{200K}{166K} = C_p\ln 2$

For N = M by extension: $\Delta S_A = C_p\ln 2$

So the change in entropy of the system doesn't depend on the path.

For N = 1: $\Delta S_u = \Delta S_A - C_p \frac{200-100}{200}$

For N = 2: $\Delta S_u = \Delta S_A - C_p \frac{150-100}{150} - C_p \frac{200-150}{200}$

For N = 3: $\Delta S_u = \Delta S_A - C_p \frac{133-100}{133} - C_p \frac{166-133}{166} - C_p \frac{200-166}{200}$

For N = M: $\Delta S_u = \Delta S_A - C_p \sum_j^N \frac{100(1+j/N)-100(1+(j-1)/N)}{100(1+j/N)} = -C_p \sum_j^N \frac{1}{j+N}$

In the limit of N very large: $\Delta S_u = \Delta S_A - C_p \ln 2 = C_p \ln 2 - C_p \ln 2 = 0$

So in the limit of a quasistatic process the entropy change of the universe is zero and the change in the Gibbs free energy of the system is zero. These indicate that a quasistatic process follows a path of equilibrium processes. The plot is at the end of the document.

5.3 Problem statement Plot as a function of time for the given data the entropy of the universe, the entropy of the lead, the phase fractions, the enthalpy of the lead, the molar enthalpies of liquid and solid lead, the molar entropies of the liquid and solid lead, the Gibbs free energy of the lead, the Gibbs free energy of the liquid and solid lead, and the molar Gibbs free energies of the liquid and solid lead.

Solution The basic equations are as follows for the molar enthalpy, molar entropy, and molar Gibbs free energy of a phase and for the total enthalpy, total entropy and total Gibbs free energy of a system.

$$\overline{H}_i - \overline{H}_{0,i} = \int_{T_0}^{T} \overline{C}_{p,i} dT = a_i(T - T_0) + b_i/2(T^2 - T_0^2) \tag{1}$$

$$\overline{S}_i - \overline{S}_{0,i} = \int_{T_0}^{T} \frac{\overline{C}_{p,i}}{T} dT = a_i \ln \frac{T}{T_0} + b_i(T - T_0) \tag{2}$$

$$\overline{G}_i = \overline{H}_i - T\overline{S}_i \tag{3}$$

$$H = \sum_i n_i \overline{H}_i \tag{4}$$

$$S = \sum_i n_i \overline{S}_i \tag{5}$$

$$G = \sum_i n_i \overline{G}_i = H - TS \tag{6}$$

In the above, the subsript i indexes s for solid or l for liquid, T is temperature, $\overline{X}$ is a molar quantity, H is enthalpy, S is entropy, and G is Gibbs free energy. We will work in Joules, moles, and minutes.

The heat added to the system at constant pressure is $\dot{H}$

$$\dot{H} = \frac{10^{-3} cal}{1.4 days} \frac{1 day}{24 \cdot 60 min} \frac{4.184 J}{1 cal} = 2.08 \cdot 10^{-6} \text{J/min} \tag{7}$$

The number of moles of lead in the system is

$$n = 10^{-6} g \frac{1\text{mole Pb}}{207\text{g Pb}} = 4.83 \cdot 10^{-9} \text{moles} \tag{8}$$

First let's calculate the time it takes the solid lead to reach the melting temperature, T_m, and call this t_1, by equating the heat added to the system to the change in enthalpy of the solid as a function of temperature, Equation 1.

$$\begin{aligned} \frac{\dot{H}(t_1 - 0)}{n} &= a_s(T - T_0) + b_s/2(T^2 - T_0^2) \\ \frac{2.08 \cdot 10^{-6}\text{J/min}}{4.83 \cdot 10^{-9}\text{moles}} t_1 = 23.6(600 - 273) + 9.75 \cdot 10^{-3}/2(600^2 - 273^2) &= 7717.2\text{J/mole} \\ t_1 &= 17.9 \text{ min} \end{aligned} \tag{9}$$

The time for melting is t_2 from equating the heat addition to the latent heat of melting, $\Delta H_m = 4.81$ kJ/mole given in the problem statement.

$$\begin{aligned} \frac{\dot{H}}{n} t_2 = \frac{2.08 \cdot 10^{-6}\text{J/min}}{4.83 \cdot 10^{-9}\text{moles}} t_2 &= 4.81 \cdot 10^3\text{J/mole} \\ t_2 &= 11.2 \text{ min} \end{aligned} \tag{10}$$

The time it takes the liquid to heat to 2000K, t_3, is given by equating the heat added to the change in enthalpy of the liquid given by Equation 1.

$$\begin{aligned} \frac{\dot{H}}{n} t_3 &= a_l(T - T_m) + b_l/2(T^2 - T_m^2) \\ \frac{2.08 \cdot 10^{-6} \text{ J/min}}{4.83 \cdot 10^{-9} \text{ moles}} t_3 = 32.4(2000 - 600) - 3.1 \cdot 10^{-3}/2(2000^2 - 600^2) &= 45360 \text{ J/mole} \\ t_3 &= 105 \text{ min} \end{aligned} \tag{11}$$

For simplicity let's define the following times:

$$\begin{aligned} t_A &\equiv t_1 = 17.9 \text{ min} \\ t_B &\equiv (t_1 + t_2) = 29.1 \text{ min} \\ t_C &\equiv (t_1 + t_2 + t_3) = 134 \text{ min} \end{aligned}$$

The phase fractions are the easiest quantities to determine. They are given by the following relations:

$$f_s(t) = \begin{cases} 1 & 0 \le t \le t_A \\ -0.0893t + 2.60 & t_A \le t \le t_B \\ 0 & t_B \le t \le t_C \end{cases}$$

$$f_l(t) = \begin{cases} 0 & 0 \le t \le t_A \\ 0.0893t - 1.60 & t_A \le t \le t_B \\ 1 & t_B \le t \le t_C \end{cases}$$

In this problem we are asked to extrapolate some molar quantitities into time (temperature) ranges where the phase is unstable. In order to perform these tasks and still have agreement between, for example, the difference in molar enthalpy at the melting point, we will adopt a single relation for the temperature of the system as a function of time. However, it should be recognized that this will give the incorrect behaviour of, for example, the liquid below the melting point. So we will calculate the temperature of the system as a function of time by solving the quadratic relation between enthalpy and heat capacity in Equation 1 where i is s for the solid or l for the liquid.

$$\begin{aligned} \Delta\overline{H}_i &= \dot{H}(t)/n_i = \left[a_i(T-T_0) + b_i/2(T^2-T_0^2)\right] \\ T(t) &= \frac{-a_i \pm \sqrt{a_i^2 + 2b_i(a_iT_0 + b_i/2T_0^2 + \dot{H}t/n_i)}}{b} \end{aligned} \tag{12}$$

The solution to the quadratic equation produces two roots. Only the physical one is given for each case to yeild the following expression with substitution of the appropriate values.

$$T(t) = \begin{cases} -2420 + \sqrt{7.26\cdot 10^6 + 88300t} & 0 \le t \le t_A \\ 600K & t_A \le t \le t_B \\ 10500 - \sqrt{1.07\cdot 10^8 - 2.78\cdot 10^5 t} & t_B \le t \le t_C \end{cases} \tag{13}$$

Let's first simplify the problem by calculating the standard state molar enthalpy and molar entropy of the liquid phase. We know that the molar enthalpy of the liquid is equal to the molar enthalpy of the solid plus the molar enthalpy of transformation at (and only at) the transformation temperature. From this is is possible to work backward to calculate the standard state molar enthalpy at 273K. But as we've adopted a common temperature-time relation for the whole system this means that:

$$\begin{aligned} \overline{S}_{l,0} &= \frac{\Delta\overline{H}_m}{T_m} \\ &= \frac{4810}{600} = 8.02\text{J/mole K} \end{aligned} \tag{14}$$

$$\overline{H}_{l,0} = \Delta\overline{H}_m = 4810\text{J/mole}$$

Now the relationships for the enthalpies can be determined from Equations 1 and 4 combined with substitution of Equation 13. The total enthalpy is given by the following expression.

$$H(t) = \dot{H}t \tag{15}$$

The molar enthalpy of the liquid is given by the following.

$$\overline{H}_s(t) = \begin{cases} \frac{\dot{H}}{n}t = 431t & 0 \le t \le t_A \\ \frac{\dot{H}}{n}t_A = 7710J/mole & t_A \le t \le t_B \\ \frac{\dot{H}}{n}(t-t_2) = 431t - 4820 & t_B \le t \le t_C \end{cases} \tag{16}$$

The molar enthalpy of the liquid is given below. Notice the inclusion of the standard state values.

$$\overline{H}_l(t) = \begin{cases} \frac{\dot{H}}{n}t + \overline{H}_{l,0} = 431t + 4810 & 0 \le t \le t_A \\ \frac{\dot{H}}{n}t_A + \overline{H}_{l,0} = 12500J/mole & t_A \le t \le t_B \\ \frac{\dot{H}}{n}(t-t_2) + \overline{H}_{l,0} = 431t - 17.2 & t_B+ \le t \le t_C \end{cases} \tag{17}$$

The entropies are determined from Equations 2 and 5 combined with substitution of Equation 13. First we'll calculate the molar entropy for the solid as a function of time.

$$\overline{S}_s(t) = \overline{S}_{s,0} + a_s \ln \frac{T}{T_0} + b_s(T - T_0) \tag{18}$$

For $0 \leq t \leq t_A$:

$$\begin{aligned}\overline{S}_s(t) = 23.6 \ln \left[\frac{-2420 + \sqrt{7.26 \cdot 10^6 + 88300t}}{273K} \right] + 9.75 \cdot 10^{-3}(-2420 + \sqrt{7.26 \cdot 10^6 + 88300t} - 273K) \\ = 23.6 \ln \left[-8.86 + \sqrt{97.4 + 1.18t} \right] + \sqrt{690 + 8.39t} - 26.3\end{aligned} \tag{19}$$

For $t_A \leq t \leq t_B$:

$$\begin{aligned}\overline{S}_s(t) = 23.6 \ln \left[\frac{600}{273} \right] + 9.75 \cdot 10^{-3}(600 - 273) \\ = 21.8\text{J/mole K}\end{aligned} \tag{20}$$

For $t_B + \leq t \leq t_C$:

$$\begin{aligned}\overline{S}_s(t) = 23.6 \ln \left[\frac{10500 - \sqrt{1.07 \cdot 10^8 - 2.78 \cdot 10^5 t}}{273} \right] + 9.75 \cdot 10^{-3} \times \\ (10500 - \sqrt{1.07 \cdot 10^8 - 2.78 \cdot 10^5 t} - 273) \\ = 23.6 \ln \left[38.5 - \sqrt{1440 - 3.73t} \right] + \sqrt{10200 - 26.4t} + 99.7\end{aligned} \tag{21}$$

So in summary the molar entropy of the solid phase is given below.

$$\overline{S}_s(t) = \begin{cases} 23.6 \ln \left[-8.86 + \sqrt{97.4 + 1.18t} \right] + \sqrt{690 + 8.39t} - 26.3 & 0 \leq t \leq t_A \\ 21.8\text{J/mole K} t_A \leq t \leq t_B \\ 23.6 \ln \left[38.5 - \sqrt{1440 - 3.73t} \right] + \sqrt{10200 - 26.4t} + 99.7 & t_B \leq t \leq t_C \end{cases} \tag{22}$$

Now we'll calculate the molar entropy for the liquid as a function of time.

$$\overline{S}_l(t) = \overline{S}_{l,0} + a_l \ln \left[\frac{T}{T_0} \right] + b_l(T - T_0) \tag{23}$$

For $0 \leq t \leq t_A$:

$$\begin{aligned}\overline{S}_l(t) = 8.02 + 32.4 \ln \left[\frac{-2420 + \sqrt{7.26 \cdot 10^6 + 88300t}}{273} \right] \\ -3.1 \cdot 10^{-3}(-2420 + \sqrt{7.26 \cdot 10^6 + 88300t} - 273) \\ = 32.4 \ln \left[-8.86 + \sqrt{97.4 + 1.18t} \right] - \sqrt{69.8 + 0.849t} + 16.4\end{aligned} \tag{24}$$

For $t_A \leq t \leq t_B$:

$$\begin{aligned}\overline{S}_l(t) = 8.02 + 32.4 \ln \left[\frac{600}{273} \right] - 3.1 \cdot 10^{-3}(600 - 273) \\ = 29.8 J/mole\end{aligned} \tag{25}$$

For $t_B \leq t \leq t_C$:

$$\begin{aligned}\overline{S}_l(t) &= 8.02 + 32.4 \ln\left[\frac{10500 - \sqrt{1.07\cdot 10^8 - 2.78\cdot 10^5 t}}{273}\right] \\ &\quad -3.1\cdot 10^{-3}(10500 - \sqrt{1.07\cdot 10^8 - 2.78\cdot 10^5 t} - 273) \\ &= 32.4 \ln\left[38.5 + \sqrt{1440 - 3.73t}\right] + \sqrt{1030 - 2.67t} - 23.7\end{aligned} \tag{26}$$

So in summary, the molar entropy of the liquid phase is given below.

$$\overline{S}_l(t) = \begin{cases} 32.4 \ln\left[-8.86 + \sqrt{97.4 + 1.18t}\right] - \sqrt{69.8 + 0.849t} + 16.4 & 0 \leq t \leq t_A \\ 29.8 J/mole & t_A \leq t \leq t_B \\ 32.4 \ln\left[38.5 + \sqrt{1440 - 3.73t}\right] + \sqrt{1030 - 2.67t} - 23.7 & t_B \leq t \leq t_C \end{cases} \tag{27}$$

Now the total entropy of the lead as a function of time comes from Equation 5. Notice directly below that for $t_A \leq t \leq t_B$ the entropy changes linearly as the phase fractions change.

$$\begin{aligned}S(t) &= n\left[8.02\frac{t}{t_2} + (21.8 - 8.02\frac{t_A}{t_2})\right] \\ &= 4.83\cdot 10^{-9}\left[8.02\frac{t}{11.2} + (21.8 - 8.02\frac{17.9}{11.2})\right] \\ &= 4.83\cdot 10^{-9}\left[0.716t + 8.98\right]\end{aligned} \tag{28}$$

So in summary, the total entropy of the lead is given below.

$$S(t) = \begin{cases} 4.83\cdot 10^{-9}\left(23.6 \ln\left[-8.86 + \sqrt{97.4 + 1.18t}\right] + \sqrt{690 + 8.39t} - 26.3\right) & 0 \leq t \leq t_A \\ 4.83\cdot 10^{-9}\left[0.716t + 8.98\right] & t_A \leq t \leq t_B \\ 4.83\cdot 10^{-9}\left(32.4 \ln\left[38.5 + \sqrt{1440 - 3.73t}\right] + \sqrt{1030 - 2.67t} - 23.7\right) & t_B \leq t \leq t_C \end{cases} \tag{29}$$

Now let's calculate the molar Gibbs free energies of each phase using Equations 3 and 13 and the expressions for the molar entropies and enthalpies of the phases.

$$\overline{G}_s(t) = \begin{cases} 431t - \left[-2420 + \sqrt{7.26\cdot 10^6 + 88300t}\right] \times & \\ \left[23.6 \ln\left[-8.86 + \sqrt{97.4 + 1.18t}\right] + \sqrt{690 + 8.39t} - 26.3\right] & 0 \leq t \leq t_A \\ 7710 - [600] \times [21.8] = -5370 J/mole & t_A \leq t \leq t_B \\ 431t - 4820 - \left[10500 - \sqrt{1.07\cdot 10^8 - 2.78\cdot 10^5 t}\right] \times & \\ \left[23.6 \ln\left[38.5 - \sqrt{1440 - 3.73t}\right] + \sqrt{10200 - 26.4t} + 99.7\right] & t_B \leq t \leq t_C \end{cases} \tag{30}$$

$$\overline{G}_l(t) = \begin{cases} 431t + 4810 - \left[-2420 + \sqrt{7.26\cdot 10^6 + 88300t}\right] \times & \\ \left[32.4 \ln\left[-8.86 + \sqrt{97.4 + 1.18t}\right] - \sqrt{69.8 + 0.849t} + 16.4\right] & 0 \leq t \leq t_A \\ 12500 - [600] \times [29.8] = -5380 J/mole & t_A \leq t \leq t_B \\ 431t - 17.2 - \left[10500 - \sqrt{1.07\cdot 10^8 - 2.78\cdot 10^5 t}\right] \times & \\ \left[32.4 \ln\left[38.5 + \sqrt{1440 - 3.73t}\right] + \sqrt{1030 - 2.67t} - 23.7\right] & t_B \leq t \leq t_C \end{cases} \tag{31}$$

Notice that at the melting point or, equivalently, for $t_A \leq t \leq t_b$, $\overline{G}_s \equiv \overline{G}_s$ by definition. But here the values are not quite equal due to rounding errors.

Now it is possible to calculate the total Gibbs free energy quantitities for the system. The total Gibbs free energy of the system is calculated using Equations 6 and 13.

$$G(t) = \begin{cases} 4.83 \cdot 10^{-9} \cdot \{431t - \left[-2420 + \sqrt{7.26 \cdot 10^6 + 88300t}\right] \times \\ \left[23.6 \ln\left[-8.86 + \sqrt{97.4 + 1.18t}\right] + \sqrt{690 + 8.39t} - 26.3\right]\} & 0 \leq t \leq t_A \\ 4.83 \cdot 10^{-9} \cdot -5370 \text{ J/mole} = -2.59 \cdot 10^{-5} \text{ J} & t_A \leq t \leq t_B \\ 4.83 \cdot 10^{-9} \cdot \{431t - 17.2 - \left[10500 - \sqrt{1.07 \cdot 10^8 - 2.78 \cdot 10^5 t}\right] \times \\ \left[32.4 \ln\left[38.5 + \sqrt{1440 - 3.73t}\right] + \sqrt{1030 - 2.67t} - 23.7\right]\} & t_B \leq t \leq t_C \end{cases} \tag{32}$$

The total Gibbs free energy of each phase is given, in general, by $G_i = nf_i\overline{G}_i$. During heating of the solid $G_s(t) = G(t)$ and $G_l = 0$ while during heating of the liquid $G_l(t) = G(t)$ and $G_s = 0$.

$$G_s(t) = \begin{cases} 4.83 \cdot 10^{-9} \cdot \{431t - \left[-2420 + \sqrt{7.26 \cdot 10^6 + 88300t}\right] \times \\ \left[23.6 \ln\left[-8.86 + \sqrt{97.4 + 1.18t}\right] + \sqrt{690 + 8.39t} - 26.3\right]\} & 0 \leq t \leq t_A \\ 4.83 \cdot 10^{-9} \cdot (479t - 14000) & t_A \leq t \leq t_B \\ 0 \text{ J} & t_B \leq t \leq t_C \end{cases} \tag{33}$$

$$G_l(t) = \begin{cases} 0 \text{ J} & 0 \leq t \leq t_A \\ 4.83 \cdot 10^{-9} \cdot (-479t + 8580) & t_A \leq t \leq t_B \\ 4.83 \cdot 10^{-9} \cdot \{431t - 17.2 - \left[10500 - \sqrt{1.07 \cdot 10^8 - 2.78 \cdot 10^5 t}\right] \times \\ \left[32.4 \ln\left[38.5 + \sqrt{1440 - 3.73t}\right] + \sqrt{1030 - 2.67t} - 23.7\right]\} & t_B \leq t \leq t_C \end{cases} \tag{34}$$

The heating proceeds in a manner approximated by reversible heat transfer between the heat bath and the body at constant pressure and temperature. The entropy change of the universe as a function of time is given by the following.

$$\begin{aligned} S_{universe}(t) &= S_{bath}(t) + S_{Pb}(t) \\ &= S_{bath,0} + \Delta S_{bath}(t) + S_{Pb}(t) \\ &= S_{bath,0} - \frac{\Delta H_{Pb}(t)}{T_{bath}} + S_{Pb}(t) \\ &= S_{bath,0} - \frac{2.08 \cdot 10^{-6} t}{2000} + S_{Pb}(t) \\ &= S_{bath,0} - 1.04 \cdot 10^{-9} t + S_{Pb}(t) \end{aligned} \tag{35}$$

$$S_{universe} = \begin{cases} S_{bath,0} - 1.04 \cdot 10^{-9} t + \\ 4.83 \cdot 10^{-9} \left(23.6 \ln\left[-8.86 + \sqrt{97.4 + 1.18t}\right] + \sqrt{690 + 8.39t} - 26.3\right) & 0 \leq t \leq t_A \\ S_{bath,0} - 1.04 \cdot 10^{-9} t + \\ 4.83 \cdot 10^{-9} \left[0.716t + 8.98\right] & t_A \leq t \leq t_B \\ S_{bath,0} - 1.04 \cdot 10^{-9} t + \\ 4.83 \cdot 10^{-9} \left(32.4 \ln\left[38.5 + \sqrt{1440 - 3.73t}\right] + \sqrt{1030 - 2.67t} - 23.7\right) & t_B \leq t \leq t_C \end{cases} \tag{36}$$

The plots are all presented at the end of this document.

5.4 Second Law Haiku

Damned oil companies
Sweet perpetual mobile
Second Law foiled thee

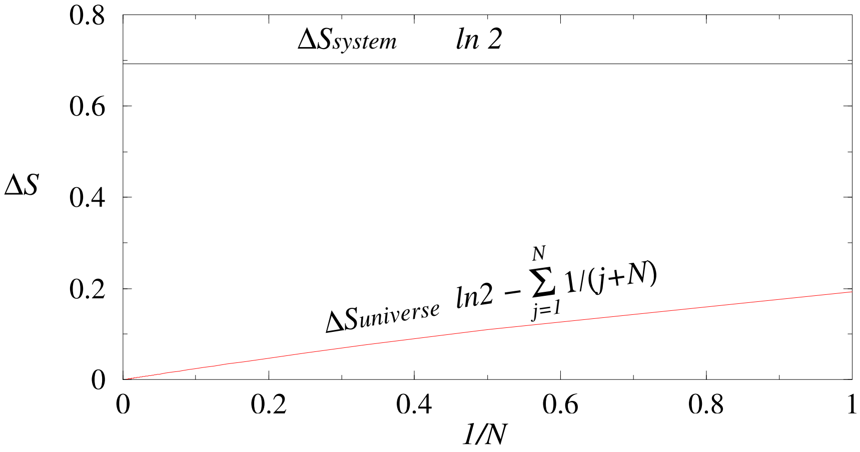

Figure 1: ΔS_u and ΔS_{sys} vs. 1/N (5.2)

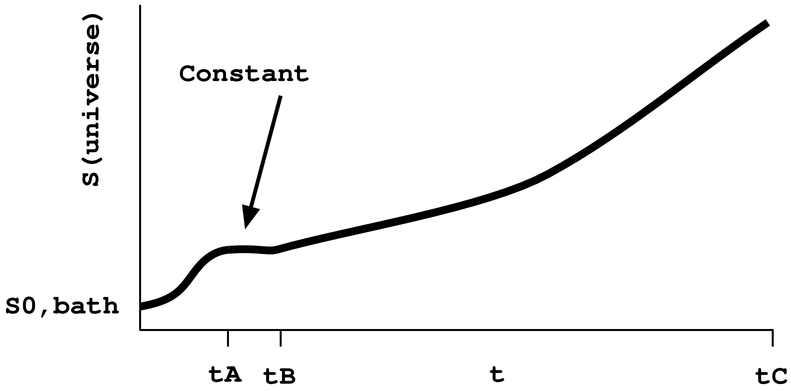

Figure 2: $S_{universe}$ versus time (5.3-1)

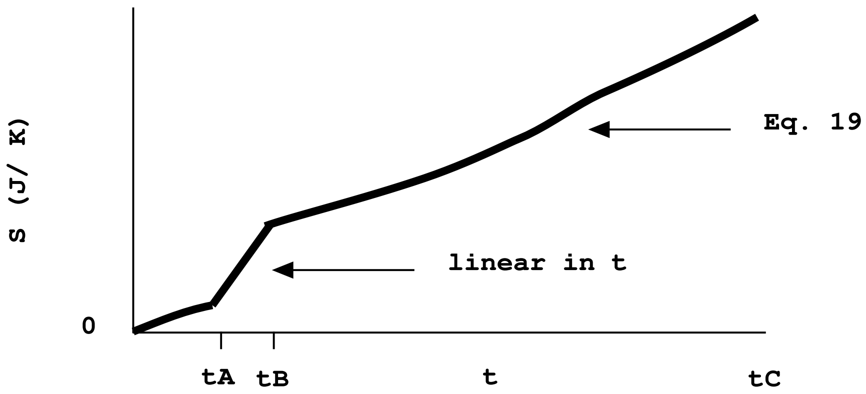

Figure 3: S_{Pb} versus time (5.3-2)

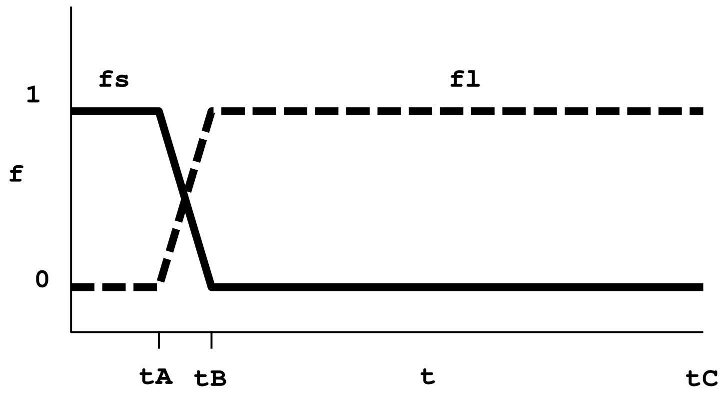

Figure 4: f versus time (5.3-3)

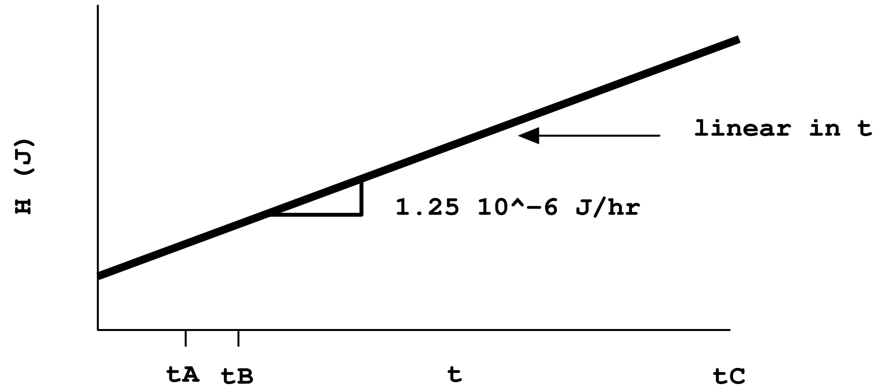

Figure 5: H_{Pb} versus time (5.3-4)

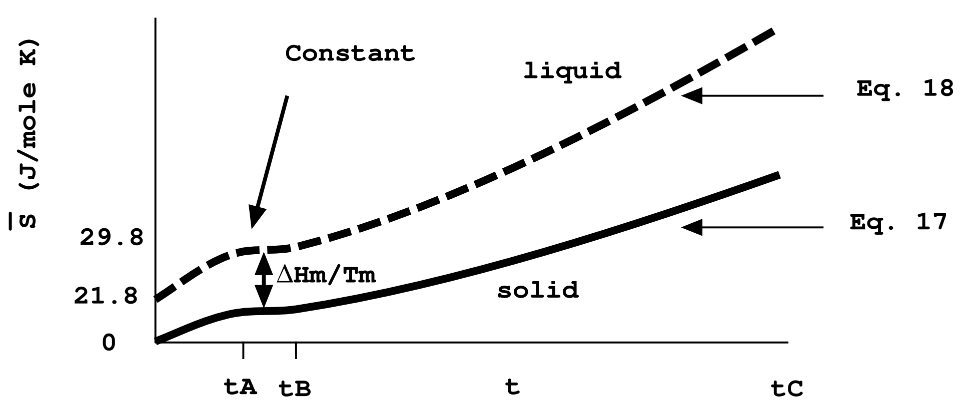

Figure 6: $\overline{S}_s$ and $\overline{S}_l$ versus time (5.3-5 and 5.3-6)

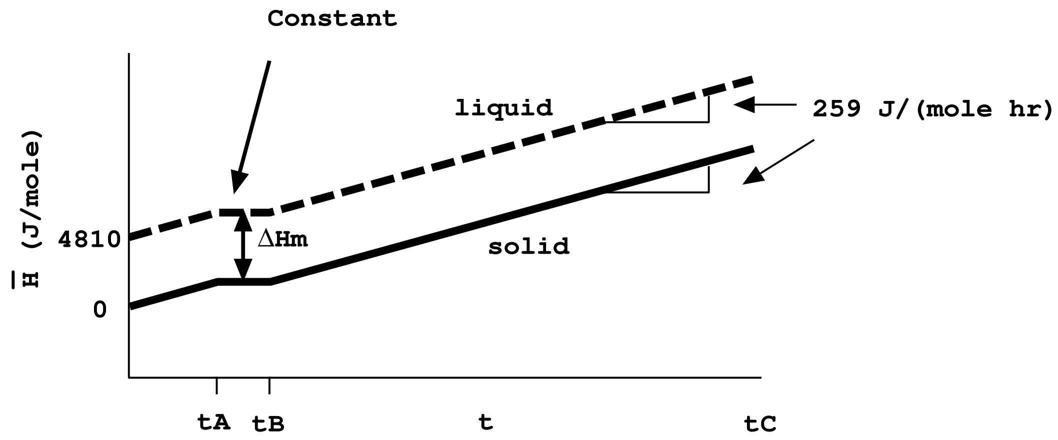

Figure 7: $\overline{H}_s$ and $\overline{H}_l$ versus time (5.3-7 and 5.3-8)

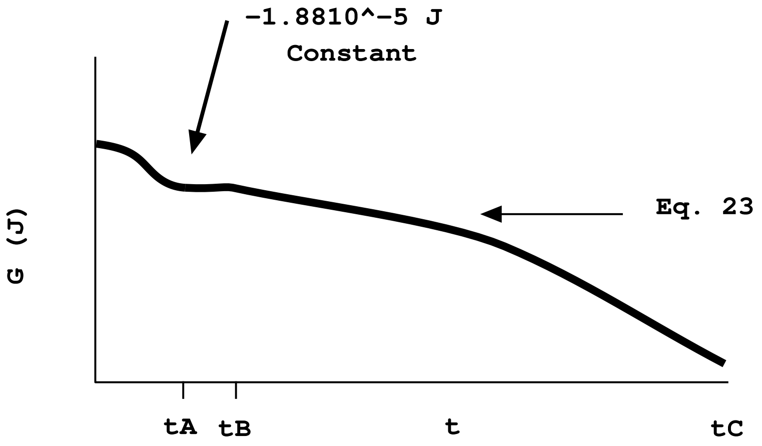

Figure 8: G_{Pb} versus time (5.3-9)

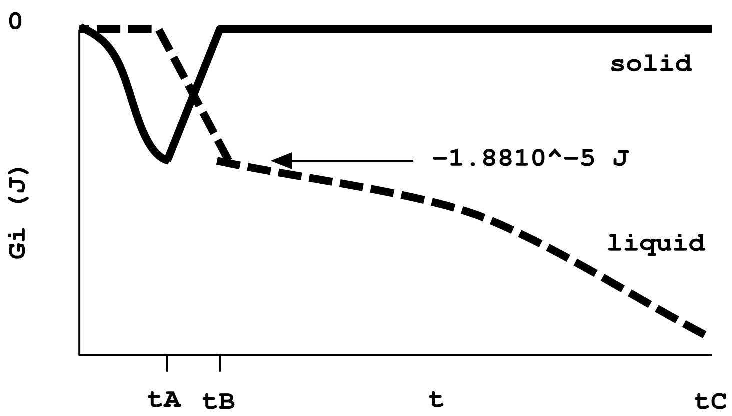

Figure 9: G_l and G_s versus time (5.3-10 and 5.3-11)

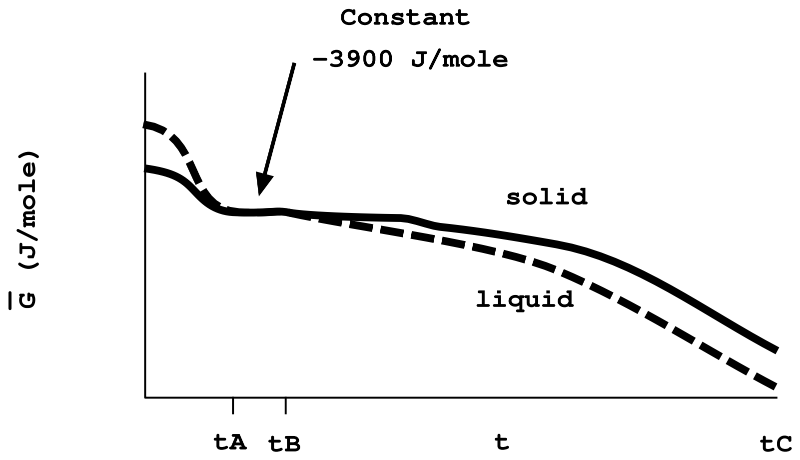

Figure 10: $\overline{G}_s$ and $\overline{G}_l$ versus time (5.3-12 and 5.3-13)