7/ (i) $p(E) = A e^{-E/k_B T}$ $\quad E = \{0, \varepsilon\}$

$\therefore$ Since $\sum_i p(E_i) = 1$ since a probability distribution

$\Rightarrow p(0) + p(\varepsilon) = 1$

$\therefore A\left(e^{-0} + e^{-\varepsilon/k_B T}\right) = 1$

$$\therefore \boxed{A = \frac{1}{1 + e^{-\varepsilon/k_B T}}}$$

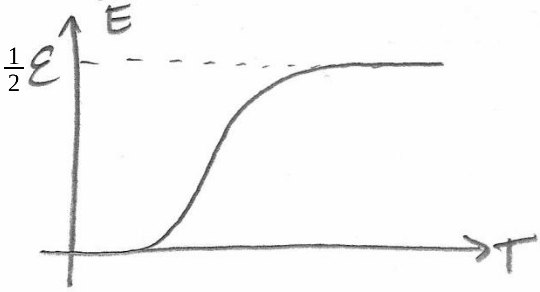
(ii) $$\bar{E} = \sum_i E_i p(E_i) = \underbrace{0}_{E=0} + \underbrace{\boxed{\frac{\varepsilon e^{-\varepsilon/k_B T}}{1 + e^{-\varepsilon/k_B T}}}}_{E=\varepsilon}$$

Since $p(E_i) = \dfrac{e^{-E_i/k_B T}}{1 + e^{-\varepsilon/k_B T}}$ So: $\boxed{\bar{E} = \dfrac{\varepsilon}{e^{\varepsilon/k_B T} + 1}}$

(iii) $$\bar{E} = \frac{\varepsilon}{e^{\varepsilon/k_B T} + 1}$$

when $T \to 0$ $\quad e^{\varepsilon/k_B T} \to \infty$ $\quad \therefore \bar{E} \to 0$

when $T \to \infty$ $\quad e^{\varepsilon/k_B T} \to 0$ $\quad \therefore \bar{E} \to \frac{1}{2}\varepsilon$



(iv) Einstein's model of average energy of thermal motion of a solid

a) $$\boxed{\bar{E} = \frac{hf}{e^{hf/k_BT} - 1}}$$

when $T \to 0$, $e^{hf/k_BT} \to \infty$ $\therefore$ $\bar{E} \to 0$

when $T \to \infty$, $e^{hf/k_BT} \to e^0 \to 1$ $\therefore$ $\bar{E} \to \infty$

Now $$\frac{d\bar{E}}{dT} = \frac{-hf}{(e^{hf/k_BT} - 1)^2} \times e^{hf/k_BT} \times \left(-\frac{hf}{k_BT^2}\right)$$

$$= \left(\frac{hf}{k_BT}\right)^2 k_B \frac{e^{hf/k_BT}}{(e^{hf/k_BT} - 1)^2}$$

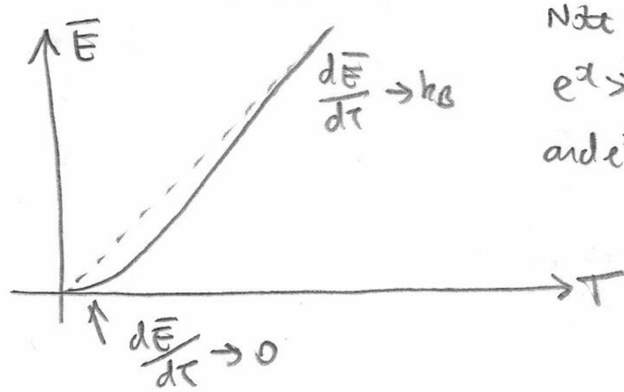
$$= \boxed{\frac{k_B x^2 e^x}{(e^x - 1)^2}} \quad \text{where } x = \frac{hf}{k_BT}$$

when $T \to \infty$, $x \to 0$ so $e^x = 1 + x + \frac{x^2}{2} + \dots$
$\to 1 + x$. $\therefore e^x - 1 \to x$

So $$\frac{d\bar{E}}{dT} \to \frac{k_B x^2 (1+x)}{x^2} \to k_B(1+x)$$

and if $x \to 0$, $\frac{d\bar{E}}{dT} \to k_B$ i.e. constant gradient.

So:



Note when $T \to 0$, $x \to \infty$
$e^x \gg 1$ and $e^x \gg x^2$ $\therefore$ $\frac{d\bar{E}}{dT} \to \frac{k_B x^2}{e^x}$
$\to 0$

b) So $C = 3N_A \frac{d\bar{E}}{dT}$ Molar heat capacity

$$\therefore \quad C = 3N_A k_B \frac{x^2 e^x}{(e^x - 1)^2} \qquad x = \frac{hf}{k_B T}$$

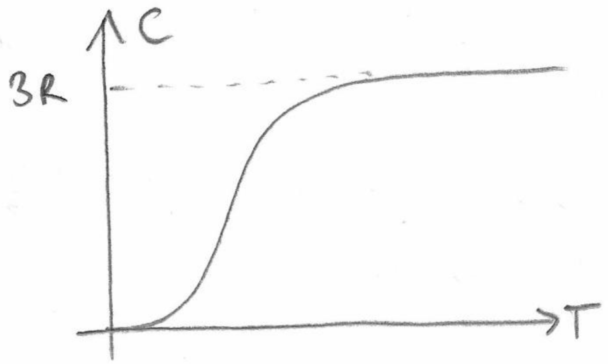
Now $R = N_A k_B$

$$\therefore \quad \boxed{C = \frac{3R\, x^2 e^x}{(e^x-1)^2}}$$

As discussed above, as $T \to \infty$, $x \to 0$

and $e^x \to 1 + x$ $\therefore$ $\boxed{C \to 3R}$

when $T \to 0$, $x \to \infty$ and $\boxed{C \to 0}$



$C = 3R$ is the 'Dulong & Petit law', which is true at $x \to 0$

ie $\frac{hf}{k_B T} \ll 1$

$\therefore$ $\boxed{T \gg \frac{hf}{k_B}}$

For various elements the 'Einstein frequency' is:

Au	0.286×10^{13} Hz
Cu	0.577 "
Fe	0.789 "
C	3.745 "
Si	1.083 "

{ Note Einstein's model is only approximate. Debye theory assumes a spectrum of possible vibration frequencies }.