2. The partition function is, for one oscillator:

$$Z_1 = \sum_i e^{-\beta\epsilon_i} = 1 + e^{-\beta\epsilon}.$$

Assuming that the oscillators are distinguishable and non-interacting,

$$Z_N = (Z_1)^N = (1 + e^{-\beta\epsilon})^N$$

So

$$F = -kT \ln Z_N$$

$$F = -NkT \ln(1 + e^{-\beta\epsilon}) = -NkT \ln\left(1 + e^{-\epsilon/kT}\right)$$

$$S = -\left.\frac{\partial f}{\partial T}\right|_{N,V} = +Nk\left[\frac{T\left(-\frac{\epsilon}{k}\right)e^{-\epsilon/kT}\left(-\frac{1}{T^2}\right)}{1 + e^{-\epsilon/kT}} + \ln\left(1 + e^{-\epsilon/kT}\right)\right]$$

$$\rightarrow \quad S = +Nk\left[\frac{(\beta\epsilon)e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} + \ln\left(1 + e^{-\beta\epsilon}\right)\right]$$

$$\rightarrow \quad P = -\left.\frac{\partial f}{\partial V}\right|_{N,T} = 0.$$

$$\rightarrow \quad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = -kT \ln\left(1 + e^{-\beta\epsilon}\right)$$

$$\rightarrow \quad C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V}$$

note: $\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} = \frac{-\beta}{T}\frac{\partial}{\partial \beta}$. So $C_V = -\beta\left(\frac{\partial S}{\partial \beta}\right)_{N,V}$

$$C_v = -\beta \frac{\partial}{\partial \beta}\left[Nk\left\{ \frac{\beta\epsilon e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}} + \ln\left(1+e^{-\beta\epsilon}\right)\right\}\right]$$

$$C_v = -Nk\beta \left[\frac{(1+e^{-\beta\epsilon})\,\epsilon\left[\beta(-\epsilon)e^{-\beta\epsilon} + e^{-\beta\epsilon}\right] - \beta\epsilon e^{-\beta\epsilon}\left[-\epsilon e^{-\beta\epsilon}\right]}{(1+e^{-\beta\epsilon})^2} \right.$$

$$\left. + \frac{-\epsilon e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}}\right]$$

$$C_v = -Nk\beta \left[\frac{e^{-\beta\epsilon}}{(1+e^{-\beta\epsilon})^2}\left((1+e^{-\beta\epsilon})\,\epsilon(1-\beta\epsilon) + \beta\epsilon^2 e^{-\beta\epsilon}\right) - \frac{\epsilon e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}}\right]$$

$$C_v = -Nk\beta \left[\frac{e^{-\beta\epsilon}}{(1+e^{-\beta\epsilon})^2}\left(\epsilon - \beta\epsilon^2 + \epsilon e^{-\beta\epsilon} - \beta\epsilon^2 e^{-\beta\epsilon} + \beta\epsilon^2 e^{-\beta\epsilon}\right) - \frac{\epsilon e^{-\beta\epsilon}(1+e^{-\beta\epsilon})}{(1+e^{-\beta\epsilon})^2}\right]$$

$$C_v = -Nk\beta \left[\frac{\epsilon e^{-\beta\epsilon}(1-\beta\epsilon+e^{-\beta\epsilon}) - \epsilon e^{-\beta\epsilon}(1+e^{-\beta\epsilon})}{(1+e^{-\beta\epsilon})^2}\right.$$

$$C_v = \frac{-Nk\beta\epsilon e^{-\beta\epsilon}}{(1+e^{-\beta\epsilon})^2}\left[1-\beta\epsilon + e^{-\beta\epsilon} - 1 - e^{-\beta\epsilon}\right]$$

$$\boxed{C_v = \frac{Nk(\beta\epsilon)^2 e^{-\beta\epsilon}}{(1+e^{-\beta\epsilon})^2}}$$

3. a) • Note carefully that there are a total of $(g_1 + g_2)$ states available to the system.

• By definition, w_i is the probability of being in a state belonging to group i.

• Since the g_i states of group i are all equally likely, then the probability of being in any particular group i state is $\left(\frac{w_i}{g_i}\right)$.

• To confirm that all the probabilities are properly normalized, we write: $$g_1\left(\frac{w_1}{g_1}\right) + g_2\left(\frac{w_2}{g_2}\right) = w_1 + w_2 = 1.$$

So, $S = -k \sum_i P_i \ln P_i$ where the sum is over <u>all</u> states.

$$S = -k\left[\underbrace{\left(\frac{w_1}{g_1}\right)\ln\left(\frac{w_1}{g_1}\right) + \cdots + \left(\frac{w_1}{g_1}\right)\ln\left(\frac{w_1}{g_1}\right)}_{g_1 \text{ times}} + \underbrace{\left(\frac{w_2}{g_2}\right)\ln\left(\frac{w_2}{g_2}\right) + \cdots + \left(\frac{w_2}{g_2}\right)\ln\left(\frac{w_2}{g_2}\right)}_{g_2 \text{ times}}\right]$$

$$S = -k\left[g_1\left(\frac{w_1}{g_1}\right)\ln\left(\frac{w_1}{g_1}\right) + g_2\left(\frac{w_2}{g_2}\right)\ln\left(\frac{w_2}{g_2}\right)\right]$$

$$S = -k\left[w_1 \ln\left(\frac{w_1}{g_1}\right) + w_2 \ln\left(\frac{w_2}{g_2}\right)\right].$$

<u>confirmed!</u>

3b. ∘ plug in $w_i = \frac{g_i}{Z} e^{-\beta \epsilon_i}$. This follows because the probability of being in a particular state which has energy ϵ_i is $\frac{1}{Z} e^{-\beta \epsilon_i}$, and there are g_i such states.

∘ note also that $Z = g_1 e^{-\beta \epsilon_1} + g_2 e^{-\beta \epsilon_2}$

∘ write Z as

$$Z = g_1 e^{-\beta \epsilon_1} \left[1 + \left(\frac{g_2}{g_1}\right) e^{-\beta \epsilon_2 + \beta \epsilon_1} \right]$$

$$Z = g_1 e^{-\beta \epsilon_1} \left[1 + \left(\frac{g_2}{g_1}\right) e^{-x} \right]$$

with $x \equiv \beta(\epsilon_2 - \epsilon_1)$.

$$-\frac{S}{k} = \frac{g_1}{Z} e^{-\beta\epsilon_1} \ln\left[\frac{g_1}{Z g_1} e^{-\beta\epsilon_1}\right] + \frac{g_2}{Z} e^{-\beta\epsilon_2} \ln\left[\frac{g_2}{Z g_2} e^{-\beta\epsilon_2}\right]$$

$$-\frac{S}{k} = \frac{g_1 e^{-\beta\epsilon_1}\left[-\beta\epsilon_1 - \ln Z\right] + g_2 e^{-\beta\epsilon_2}\left[-\beta\epsilon_2 - \ln Z\right]}{g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2}}$$

$$-\frac{S}{k} = \frac{g_1 e^{-\beta\epsilon_1}\left\{-\beta\epsilon_1 - \ln Z + \left(\frac{g_2}{g_1}\right) e^{-x}\left[-\beta\epsilon_2 - \ln Z\right]\right\}}{g_1 e^{-\beta\epsilon_1}\left(1 + \frac{g_2}{g_1} e^{-x}\right)}$$

$$-\frac{S}{k} = \frac{-\beta\epsilon_1 - \ln Z - \left(\frac{g_2}{g_1}\right) e^{-x}\beta\epsilon_2 - \frac{g_2}{g_1} e^{-x}\ln Z}{\left(1 + \frac{g_2}{g_1} e^{-x}\right)}$$

$$+\frac{S}{k} = \frac{+\beta\epsilon_1 + \ln\left[g_1 e^{-\beta\epsilon_1}\right] + \ln\left[1 + \frac{g_2}{g_1} e^{-x}\right] + \left(\frac{g_2}{g_1}\right) e^{-x}\beta\epsilon_2 + \frac{g_2}{g_1} e^{-x}\ln Z}{\left(1 + \frac{g_2}{g_1} e^{-x}\right)}$$

$$\frac{S}{k} = \frac{\cancel{\beta\epsilon_1} + \ln g_1 - \cancel{\beta\epsilon_1} + \ln\left(1 + \frac{g_2}{g_1} e^{-x}\right) + \beta\epsilon_2\left(\frac{g_2}{g_1}\right) e^{-x} + \frac{g_2}{g_1} e^{-x}\ln Z}{\left(1 + \frac{g_2}{g_1} e^{-x}\right)}$$

$$\frac{S}{k} = \frac{\ln g_1 + \ln\left[1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right] + \left(\frac{g_2}{g_1}\right)e^{-x}\left[\beta\epsilon_2 + \ln z\right]}{\left(1 + \frac{g_2}{g_1}e^{-x}\right)}$$

$$\frac{S}{k} = \frac{\ln g_1 + \ln\left[1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right] + \left(\frac{g_2}{g_1}\right)e^{-x}\left[\beta\epsilon_2 + \ln g_1 - \beta\epsilon_1 + \ln\left[1 + \frac{g_2}{g_1}e^{-x}\right]\right]}{\left(1 + \frac{g_2}{g_1}e^{-x}\right)}$$

$$\frac{S}{k} = \frac{\left(1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right)\ln g_1 + \left(1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right)\ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \left(\frac{g_2}{g_1}\right)e^{-x}\beta(\epsilon_2 - \epsilon_1)}{\left(1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right)}$$

$$\frac{S}{k} = \ln g_1 + \ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{\left(\frac{g_2}{g_1}\right)e^{-x}x}{1 + \left(\frac{g_2}{g_1}\right)e^{-x}}\underbrace{\left[\frac{e^{x}}{e^{x}}\right]\left(\frac{\frac{g_1}{g_2}}{\frac{g_1}{g_2}}\right)}_{=1}$$

$$\frac{S}{k} = \ln g_1 + \ln\left[1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right] + \frac{x}{\left(\frac{g_1}{g_2}\right)e^{x} + 1}$$

$$S = k\left[\ln g_1 + \ln\left\{1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right\} + \frac{x}{1 + \left(\frac{g_1}{g_2}\right)e^{x}}\right]$$

Check

3c)

$$Z = g_1 e^{-\epsilon_1/kT}\left[1 + \left(\frac{g_2}{g_1}\right) e^{-\frac{(\epsilon_2-\epsilon_1)}{kT}}\right]$$

$$F = -kT\ln Z = -kT\left[\ln g_1 - \frac{\epsilon_1}{kT} + \ln\left\{1 + \left(\frac{g_2}{g_1}\right) e^{-\frac{(\epsilon_2-\epsilon_1)}{kT}}\right\}\right]$$

$$F = -kT\ln g_1 + \epsilon_1 - kT\ln\left\{1 + \left(\frac{g_2}{g_1}\right) e^{-\frac{(\epsilon_2-\epsilon_1)}{kT}}\right\}$$

$$S = -\frac{\partial F}{\partial T} = -\left[-k\ln g_1 - \left\{\frac{Tk\left(\frac{g_2}{g_1}\right)\left(-\frac{(\epsilon_2-\epsilon_1)}{kT}\right) e^{-\frac{(\epsilon_1-\epsilon_2)}{kT}}\left(-\frac{1}{T^2}\right)}{1+\left(\frac{g_2}{g_1}\right) e^{-\frac{(\epsilon_2-\epsilon_1)}{kT}}}\right.\right.$$

$$\left.\left. + k\ln\left\{1 + \left(\frac{g_2}{g_1}\right) e^{-\frac{(\epsilon_2-\epsilon_1)}{kT}}\right\}\right\}\right]$$

$$S = k\ln g_1 + \left[\frac{k\left(\frac{g_2}{g_1}\right)\left(\frac{\epsilon_2-\epsilon_1}{kT}\right) e^{-x}}{1+\left(\frac{g_2}{g_1}\right) e^{-\frac{(\epsilon_2-\epsilon_1)}{kT}}}\right] + k\ln\left\{1 + \left(\frac{g_2}{g_1}\right) e^{-\frac{(\epsilon_2-\epsilon_1)}{kT}}\right\}$$

$$S = k\ln g_1 + \left[\frac{k\left(\frac{g_2}{g_1}\right) x e^{-x}}{1+\left(\frac{g_2}{g_1}\right) e^{-x}}\left(\frac{\frac{g_1}{g_2}}{\frac{g_1}{g_2}}\right)\right] + k\ln\left\{1 + \left(\frac{g_1}{g_2}\right) e^{-x}\right\}$$

$$S = k \ln g_1 + k \ln\left[1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right] + \frac{k x e^{-x}}{\left(\frac{g_1}{g_2}\right) + e^{-x}}\left(\frac{e^{x}}{e^{x}}\right)$$

$$S = k \ln g_1 + k \ln\left[1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right] + \left[\frac{k x}{\left(\frac{g_1}{g_2}\right)e^{x} + 1}\right]$$

Confirmed!

d) as $T \to$, $x \to \infty$, so

$$k \ln\left[1 + \left(\frac{g_2}{g_1}\right)e^{-x}\right] \to k \ln(1) = 0.$$

and

$$\frac{x}{1 + \left(\frac{g_1}{g_2}\right)e^{x}} \to \left(\frac{\infty}{\infty}\right) \to \frac{1}{\left(\frac{g_1}{g_2}\right)e^{x}} \quad \text{by L'Hôpital's rule}$$

$$\to 0.$$

So yes,

$$S \to k \ln g_1 .$$

The Third law doesn't apply to systems with degenerate ground states!