Using the data (heat capacity) from book or internet and also $\Delta H_{fus}(I_2)$ = 15.524 kJ/mol at 387 K and $\Delta H_{vap}(I_2)$ = 41.57 kJ/mol at 457 K: a) calculate the heat required to bring one mole of iodine from 0 K to 500 K; b) calculate the absolute entropy of iodine at 500 K.

Solution: Temperature dependencies of molar heat capacity (J·mol^{-1}·K^{-1}) of iodine are:

1) in solid state, $C^{\circ}_{p(s)}(T) = 40.12 + 0.0498 \cdot T;\ T = 298 - 387$ K;

T, K	15	21	30	36	45	60	75	90
C°$_p$, J·mol^{-1}·K^{-1}	9.2	19.7	25.6	31.4	35.2	40.2	43.6	45.8
T, K	105	120	135	150	180	200	250	300
C°$_p$, J·mol^{-1}·K^{-1}	46.8	47.6	48.2	49.0	50.2	51.2	53.6	55.1

According to the Debye T^3 law, dependency of the heat capacity of solids at the low temperatures can be shown as $C^{\circ}_{p(s)}(T) = k \cdot T^3;\ T = 0 - 15$ K.

The coefficient k can be calculated as: $k = \dfrac{C^{\circ}_p(15)}{15^3} = \dfrac{9.2}{3375} = 2.726 \cdot 10^{-3}\ \dfrac{\text{J}}{\text{mol} \cdot \text{K}^4}$.

2) in gaseous state, $C^{\circ}_{p(g)}(T) = 37.4 + 5.9 \cdot 10^{-4} \cdot T - \dfrac{7.1 \cdot 10^4}{T^2};\ T = 298 - 1000$ K;

As you know, iodine sublimes (becomes a gas directly from the solid phase) instead of melting. Latent heat of sublimation is equal to the sum of latent heats of fusion and vaporization:

$\Delta H_{sub}(I_2)$ = 15.524 + 41.57 = 57.094 kJ/mol = 57,094 J/mol.

a) The amount of heat Q, required for the heating of one mole of iodine from 0 K to 500 K at constant pressure (1 atm) can be calculated as the change of standard molar enthalpy, which depends from the heat capacity of iodine and heat of phase transition (latent heat of sublimation):

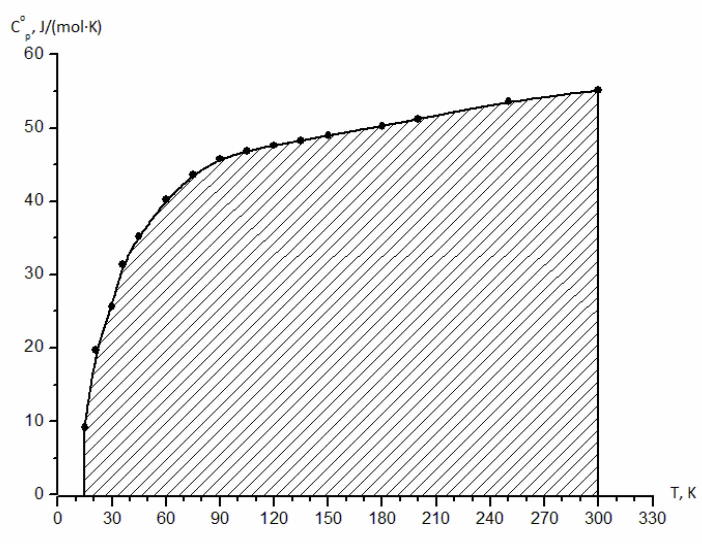
$Q = \Delta H^{\circ}_{500} = \int_0^{T_S} C^{\circ}_{p(s)}(T)\,dT + \Delta H_{sub} + \int_{T_S}^{500} C^{\circ}_{p(g)}(T)\,dT$, where T_s is the temperature of sublimation of iodine, which is equal to the melting point (387 K).

As you see, dependency of molar heat capacity of solid iodine in the temperature range from 15 K to 300 K is available only in the tabular form. Thus, we must calculate the value of $\int_{15}^{300} C^{\circ}_{p(s)}(T)\,dT$ by graphical integration, which is based on determining of the area under the curve $C^{\circ}_{p(s)}(T)$ from 15 K to 300 K.

Then, $Q = \int_0^{15} C^{\circ}_{p(s)}(T)\,dT + (H^{\circ}_{300} - H^{\circ}_{15}) + \int_{300}^{387} C^{\circ}_{p(s)}(T)\,dT + \Delta H_{sub} + \int_{387}^{500} C^{\circ}_{p(g)}(T)\,dT$, where $(H^{\circ}_{300} - H^{\circ}_{15})$ is the value, determined by graphical integration.

First integral is equal to: $\int_0^{15} C^{\circ}_{p(s)}(T)\,dT = \int_0^{15} k \cdot T^3 dT = \dfrac{k}{4} \cdot T^4 \Big|_0^{15} = \dfrac{2.726 \cdot 10^{-3}}{4} \cdot 15^4 = 34.5\ \dfrac{\text{J}}{\text{mol}}$.

Graphical integration gives the value of $\int_{15}^{300} C^{\circ}_{p(s)}(T)\,dT = (H^{\circ}_{300} - H^{\circ}_{15}) = 13315.25\ \dfrac{\text{J}}{\text{mol}}$ (graph of the function $C^{\circ}_{p(s)} = f(T)$ is shown below).



And the rest of integrals are: $\int_{300}^{387} C^{\circ}_{p(s)}(T)\,dT = \int_{300}^{387}(40.12 + 0.0498\cdot T)dT = \left(40.12\cdot T + \frac{0.0498}{2}\cdot T^2\right)\Bigg|_{300}^{387} =$

$= 40.12\cdot(387-300) + 0.0249\cdot(387^2 - 300^2) = 4978.7\ \frac{\text{J}}{\text{mol}}$.

$$\int_{387}^{500} C^{\circ}_{p(g)}(T)\,dT = \int_{387}^{500}\left(37.4 + 5.9\cdot10^{-4}\cdot T - \frac{7.1\cdot10^4}{T^2}\right)dT = \left(37.4\cdot T + \frac{5.9\cdot10^{-4}}{2}\cdot T^2 + \frac{7.1\cdot10^4}{T}\right)\Bigg|_{387}^{500} =$$

$$= 37.4\cdot(500-387) + 2.95\cdot10^{-4}\cdot(500^2 - 387^2) + 7.1\cdot10^4\cdot\left(\frac{1}{500} - \frac{1}{387}\right) = 4214.3\ \frac{\text{J}}{\text{mol}}.$$

Then, Q = 34.5 + 13315.25 + 4978.7 + 57,094 + 4214.3 = 79636.75 J = 79.64 kJ.

Answer: 79.64 kJ.

b) The absolute entropy of iodine at 500 K can be calculated as the standard entropy of solid iodine at 298 K plus change of absolute entropy in the range from 298 K to 500 K, which depends from the heat capacity of iodine and heat of phase transition (latent heat of sublimation):

$S^{\circ}_{500} = S^{\circ}_{298} + \Delta S^{\circ}_{500} = S^{\circ}_{298} + \int_{298}^{T_S} \frac{C^{\circ}_{p(s)}(T)}{T}dT + \frac{\Delta H_{sub}}{T_S} + \int_{T_S}^{500} \frac{C^{\circ}_{p(g)}(T)}{T}dT$, where $S^{\circ}_{298} = 116.14\ \frac{\text{J}}{\text{mol}\cdot\text{K}}$ is the standard entropy of solid iodine at 298 K.

First integral is equal to: $\int_{298}^{T_S} \frac{C^{\circ}_{p(s)}(T)}{T}dT = \int_{298}^{387} \frac{40.12 + 0.0498\cdot T}{T}dT = \int_{298}^{387}\left(\frac{40.12}{T} + 0.0498\right)dT =$

$= (40.12\cdot\ln T + 0.0498\cdot T)\Big|_{298}^{387} = 40.12\cdot\ln\frac{387}{298} + 0.0498\cdot(387-298) = 14.92\ \frac{\text{J}}{\text{mol}\cdot\text{K}}$. And the second integral is: $\int_{T_S}^{500} \frac{C^{\circ}_{p(g)}(T)}{T}dT = \int_{387}^{500}\left(\frac{37.4}{T} + 5.9\cdot10^{-4} - \frac{7.1\cdot10^4}{T^3}\right)dT = \left(37.4\cdot\ln T + 5.9\cdot10^{-4}\cdot T + \frac{7.1\cdot10^4}{2\cdot T^2}\right)\Bigg|_{387}^{500} =$

$$= 37.4\cdot\ln\frac{500}{387} + 5.9\cdot10^{-4}\cdot(500-387) + 3.55\cdot10^4\cdot\left(\frac{1}{500^2} - \frac{1}{387^2}\right) = 9.55\ \frac{\text{J}}{\text{mol}\cdot\text{K}}.$$

Then, absolute entropy of iodine at 500 K is $S^{\circ}_{500} = 116.14 + 14.92 + \frac{57{,}094}{387} + 9.55 = 288.14\ \frac{\text{J}}{\text{mol}\cdot\text{K}}$.

Answer: 288.14 J/(mol·K).