Answer all parts together.

1. Three normal modes of vibration of CO_2 have $\Theta_{vib} = 3360, 954, 1890$. The second mode is doubly degenerate. Calculate the contribution to the heat capacity of these modes at 300 K. **[2]**
2. Calculate the molar entropy of He gas at 0 K and 273.15 K, 1 bar. **[3]**
3. Express the Helmholtz energy, $A = U - TS$ in terms of the partition function. **[2]**
4. N_2 and CO are isoelectronic molecules but M-N_2 complexes are much weaker compared to M-CO complexes. Draw the MO diagram of both N_2 and CO and then explain why? (M is a transition metal ion) **[2+2+2]**
5. In the following stepwise reactions, the order of the values of rate constants is $k_1 \approx k_2 \gg k_3$. Explain in details why? **[3]**

$$[Cu(H_2O)_6]^{+2} + en \xrightarrow{k_1} [Cu(H_2O)_4\,en]^{+2} + 2\,H_2O$$ (en: ethylenediamine)

$$[Cu(H_2O)_4\,en]^{+2} + en \xrightarrow{k_2} [Cu(H_2O)_2\,(en)_2]^{+2} + 2\,H_2O$$

$$[Cu(H_2O)_2\,(en)_2]^{+2} + en \xrightarrow{k_3} [Cu(en)_3]^{+2} + 2\,H_2O$$

6. Has $FeCr_2O_4$ normal or inverse spinel structure? Explain why? **[1+1]**
7. Determine the total number of metal-metal bonds in $(\eta^4\text{-}C_4H_4)_2Fe_2(CO)_3$. **[3]**

Useful information

$$m_n = m_p = 1.67 \times 10^{-27}\ kg;\ h = 6.626 \times 10^{-34}\ \text{Js};\ c = 2.998 \times 108\ \text{ms}^{-1},$$

$$N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$$

Molar volume of an ideal gas = 22.4 L at STP.

$$\bar{C}_{V,vib} = \frac{d\langle \bar{E}_{vib} \rangle}{dT} = R(\beta h\nu)^2 \frac{\beta h\nu}{(1 - e^{-\beta h\nu})^2}$$

Monoatomic ideal gas

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi M k_B T}{h^2}\right)^{3N/2} V^N .\ g_0$$

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

Stirling's approximation: $\ln N! = N \ln N - N$