

- 1(20). Calculate  $C_{P,m}^{\circ}$  for gaseous  $\text{CO}_2$  at 298 K. The vibrational frequencies are  $\tilde{\nu}/(\text{cm}^{-1}) = 1384.86, 667.30$  (double degenerate), and  $2349.30$ .

For the Shomate equation  $C_{P,m}^{\circ}/(\text{J K}^{-1} \text{ mol}^{-1}) = A + BT + CT^2 + DT^3 + ET^2$ , the NIST data base gives  $A = 24.99735, B = 55.18696 \times 10^{-3}, C = -33.69137 \times 10^{-6}, D = 7.948387 \times 10^{-9}$ , and  $E = -0.136638 \times 10^6$  for  $\text{CO}_2$ . Calculate  $C_{P,m}^{\circ}$  from these data.

Compare the results.

- 2(30). The electronic thermal energy of a metal is given by

$$E(\text{thermal,electronic}) = \frac{3}{5}NE_{\text{F}} \left[ 1 + \left( \frac{5\pi^2}{12} \right) \left( \frac{k_{\text{B}}T}{E_{\text{F}}} \right)^2 + \dots \right]$$

Derive the equation for  $C_{V}(\text{electronic})$ .

The value of the Fermi energy can be calculated using

$$E_{\text{F}} = \left( \frac{h^2}{8m_{\text{e}}} \right) \left( \frac{3N}{\pi V_{\text{m}}} \right)^{2/3}$$

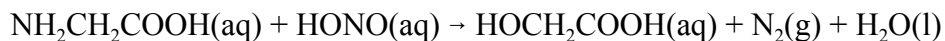
where  $m_{\text{e}} = 9.11 \times 10^{-31}$  kg. Given the density of Mg at 25 °C is  $1.74 \text{ g cm}^{-3}$ , calculate  $E_{\text{F}}$ .

Determine the value of the electronic heat capacity at 25 °C for Mg.

What fraction of the classical limit given by the Law of Dulong-Petit is the electronic heat capacity at 25 °C?

- 3(10). Starting with  $d(\Delta H) = \Delta C_p dT$ , derive the equation expressing  $\Delta_{\text{r}}H_{T_2} - \Delta_{\text{r}}H_{T_1}$  for a chemical reaction assuming the heat capacity data are given by the Shomate equation (see Question 1).

- 4(10). Calculate the difference between  $\Delta_{\text{r}}H$  and  $\Delta_{\text{r}}U$  for the chemical reaction between glycine and nitrous acid at 25 °C.



5(30). Consider the reversible, isothermal expansion of one mole of Ne acting ideally from a pressure of 10.00 bar to 1.00 bar at 25 °C. Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  for this process.

Assuming the arm of the piston from the above expansion is connected to a second piston containing one mole of He initially at 25 °C and that all of the work is used to compress the He reversibly and adiabatically, calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  for this process and calculate the final temperature.

Calculate the ratio of the final pressure to the initial pressure for the He after the compression process is completed.