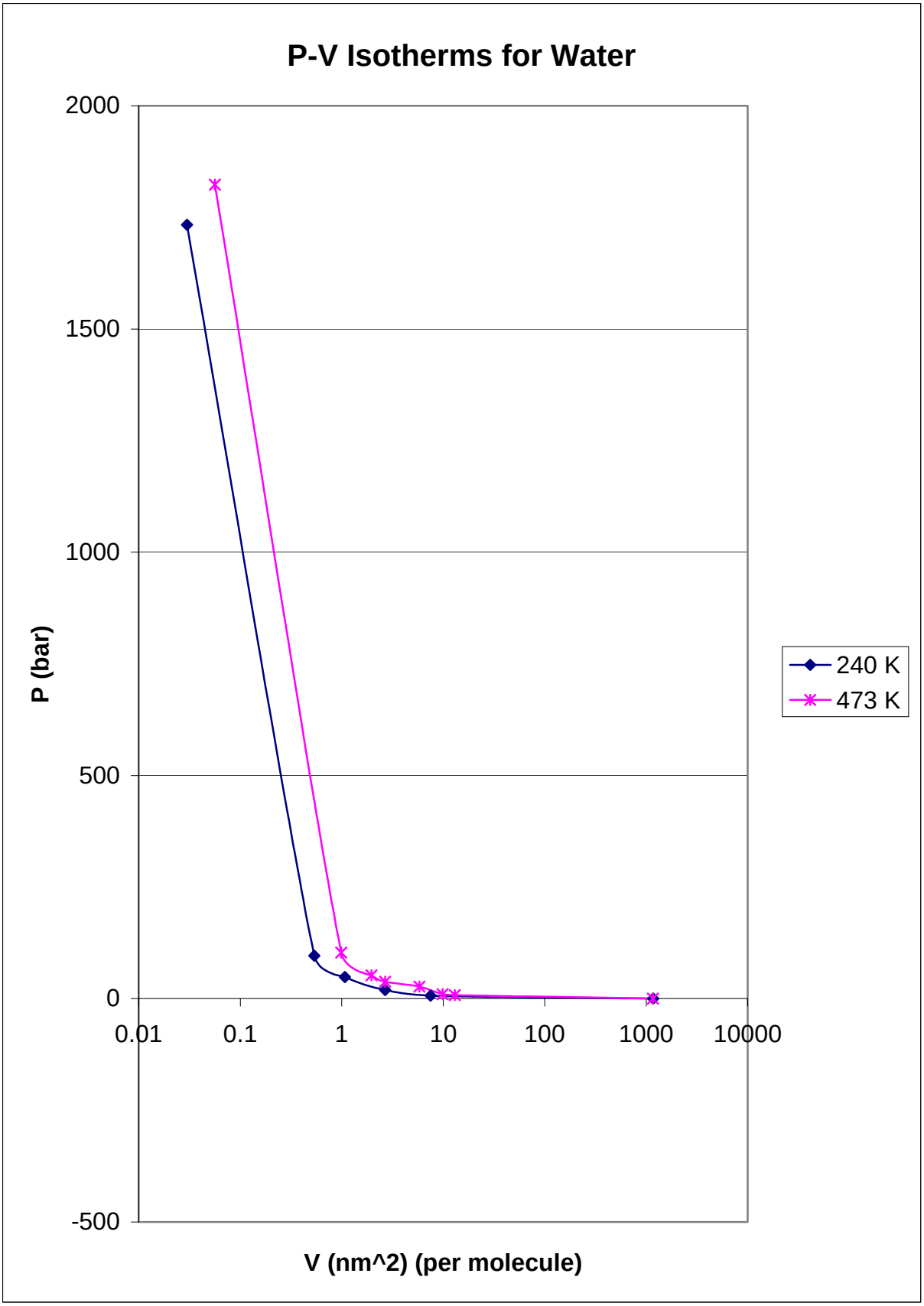
10.40 Thermodynamics **Fall 2003**
Problem Set 9

#2

Compute at least two *P-V* isotherms. See if you can find one in the liquid-vapor coexistence region. If you can find one, estimate the densities of the two phases at coexistence.

Solution:

Each isotherm is computed by choosing a temperature and then varying the periodic box volume. Each volume is a point. The pressure for each point is found by computing the mean pressure of the equilibrium data. Shown below is the data for 240 and 473 K. Ninety-three water molecules were used for the 240K data and 60 water molecules were used for the 473K behavior. Heat runs were at least 100,000 point for all runs and equilibrium runs were at least 300,000 points with many of them being 500,000 points. The box volumes where chosen so as to span the water and vapor density that the steam table gives for those temperatures. Both isotherms show behavior which is consistent with being above the critical point of the system. The system does not match the steam table data. Some reasons for this discrepancy may the small size of the system (we probably would need 900 to 2,000 water molecules since water is a structured fluid) and the short duration of the simulations. The potential that we used for the model, CHARMm22 should be able to give good predictions of the behavior of water.


P-V Isotherms for Water
2000
1500
1000
500
0
-500
P (bar)
0.01
0.1
1
10
100
1000
10000
V (nm^2) (per molecule)
240 K
473 K