

## Fisicoquímica.

### Problemario 1/3

- For steam at 500°C and 10 MPa, using the Mollier diagram,
  - Compute the Joule-Thomson coefficient  $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$
  - Compute the coefficient  $\kappa_s = \left(\frac{\partial T}{\partial P}\right)_s$
- Evaluate the difference  $\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial V}{\partial T}\right)_V$  for the ideal and van der Waals gases, and for a gas that obeys the virial equation of state.
- One hundred cubic meters of carbon dioxide initially at 150°C and 50 bar is to be isothermally compressed in a frictionless piston-and-cylinder device to a final pressure of 300 bar. Calculate
  - The volume of the compressed gas
  - The work done to compress the gas
  - The heat flow on compressionassuming carbon dioxide a. is an ideal gas, b. Obeys the principle of corresponding states, c. Obeys the Peng-Robinson equation of state.
- Ethylene at 30 bar and 100°C passes through a heater-expander and emerges at 20 bar and 150°C. There is no flow of work into or out of the heater-expander, but heat is supplied. Assuming that ethylene obeys the Peng-Robinson equation of state, compute the flow of heat into the heater-expander per mole of ethylene.



- Calculate  $\Delta A$  and  $\Delta G$  when a mole of water vapor initially at 200°C and 1 bar undergoes a cyclic process for which  $W = 145$  J.
- a) Use the equations  $C_p = \left(\frac{\partial H}{\partial T}\right)_P$ ,  $\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P}\right) = \frac{\partial}{\partial P} \left(\frac{\partial H}{\partial T}\right)$ , and  $\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V = -TV\alpha + V$  to show that  $\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$ . The volumes of substances increase approximately linearly with T, so  $\frac{\partial^2 V}{\partial T^2}$  is usually quite small. Consequently, the pressure dependence of  $C_p$  can usually be neglected unless one is dealing with high pressures.  
  
The volume of Hg in the temperature range 0°C to 100°C at 1 atm is given by  $V = V_0(1 + \alpha t + bt^2)$ , where  $\alpha = 0.18182 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ ,  $b = 0.78 \times 10^{-8} \text{ } ^\circ\text{C}^{-2}$ ,  $V_0$  is the volume at 0°C, and t is the Celsius temperature. The density of mercury at 1 atm and 0°C is 13.596 g/cm<sup>3</sup>. b) Calculate  $\left(\frac{\partial C_p}{\partial P}\right)_T$  for Hg at 25°C and 1 atm. c) Given  $C_{p,m} = 6.66 \text{ cal mol}^{-1} \text{ K}^{-1}$  for Hg at 1 atm and 25°C, estimate  $C_{p,m}$  of Hg at 25°C and 10<sup>4</sup> atm.
- Calculate  $\Delta G$  for the isothermal compression of 30.0 g of water from 1.0 atm to 100.0 atm at 25°C; neglect the variation of V with P.
- Suppose 1.00 mol of water initially at 27°C and 1 atm undergoes a process whose final state is 100°C and 50 atm. Calculate  $\Delta H$ ,  $\Delta U$ , and  $\Delta S$  considering that the temperature and pressure variations of  $\alpha$ ,  $\kappa$ , and  $C_p$  can be neglected.

# Advanced Physical Chemistry Problems V

## Thermodynamics

**J Ma**



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