Chemistry 431
Problem Set 7
Fall 2023

1. Show that $G = A + PV$.

2. For the reaction

   $CH_{4(g)} + 2\ O_{2(g)} \longrightarrow CO_{2(g)} + 2\ H_2O_{(l)}$

   use Tables 4.1 and 4.2 to determine at 25°C

   (a) The amount of heat liberated per mole at constant pressure;
   (b) The maximum amount of work obtainable from the reaction per mole;
   (c) The maximum amount of non-PV work obtainable from the reaction per mole.

3. Three moles of an ideal diatomic gas at 1.0 bar pressure and a temperature of 25.°C are taken through the following series of steps:

   (a) a free adiabatic expansion into a vacuum to double its volume;
   (b) a constant volume heating to 100.°C;
   (c) a reversible adiabatic compression to the initial volume;
   (d) a cooling at constant pressure to 25.°C.

   Calculate $\Delta U, \Delta H, \Delta S, \Delta A, \Delta G, q, w$, and $\int \frac{đq_{sys}}{T}$, for the overall process "a" + "b" +"c" +"d."

4. A certain gas obeys the equation of state

   $$P(V - nb) = nRT$$

   where b is a constant independent of P, T, V and n. Show that

   $$\left(\frac{\partial U}{\partial P}\right)_T = 0$$

   for this particular gas.

5. A certain gas obeys the van der Waals equation of state

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

where a and b are numerical constants. Derive an expression for $(\partial U/\partial S)_T$ for the van der Waals gas in terms of a, b, V, n and R.

6. Show that

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

7. For an ideal gas, show that

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma\left(\frac{P}{V}\right)$$

where $\gamma = C_P/C_V$.

8. A certain gas obeys the equation of state

$$P(V - nb) = nRT$$

where b is a numerical constant. Derive an expression for $(\partial H/\partial S)_T$ for the gas.

9. The work done on a rubber band when it is stretched by an infinitesimal length $d\ell$ owing to an applied force, F, is given by $dw = Fd\ell$.

   (a) Neglecting the volume change on stretching, show that

   $$\left(\frac{\partial U}{\partial \ell}\right)_T = F - T\left(\frac{\partial F}{\partial T}\right)_\ell$$

   (b) Experimentally, the force at constant length is given by

   $$F = \gamma T$$

   where γ is a constant. Show that

   $$\left(\frac{\partial U}{\partial \ell}\right)_T = 0$$

   (c) Since stretching orders the rubber polymer, it can be shown that

   $$(\partial S/\partial F)_T < 0$$

   i.e. there is an entropy decrease upon stretching. From this sign deduce the sign of $(\partial \ell/\partial T)_F$. Use this to predict what will happen to a rubber band with a weight hanging from it, if the temperature of the rubber is raised.

10. In addition to PV work, systems with a surface require work to form the surface. At constant volume, the expression for the reversible work to form the surface is

$$đw_{rev} = \gamma d\sigma$$

where γ is a constant called the surface tension and σ is the area of the surface that is formed. Then at constant volume, the total differential of the internal energy is given by

$$dU = TdS + \gamma d\sigma.$$

For ideal systems, the surface tension is proportional to the temperature; i.e.

$$\gamma = \kappa T$$

where κ is a proportionality constant. By generating the Helmholtz free energy and the appropriate Euler-Maxwell relation, derive an expression for $(\partial U/\partial\sigma)_T$ for an ideal system.

11. A certain gas obeys the Berthelot equation of state

$$P = \frac{nRT}{V - nb} - \frac{an^2}{TV^2}$$

where a and b are numerical constants independent of T, V, P and n. Derive an expression for $\left(\frac{\partial H}{\partial V}\right)_T$ for the Berthelot gas.

12. A certain gas obeys the equation of state

$$P = \frac{nRT}{V - nb}$$

where b is a constant. For this gas, derive an equation for $(\partial H/\partial P)_T$.

13. A certain gas obeys the equation of state

$$P = \frac{nRT}{V - nb}$$

where b is a constant. Derive an expression for $(\partial H/\partial V)_T$ for the gas.

14. A certain gas obeys the equation of state

$$P = \frac{nRT}{V - nb}$$

where b is a constant. Determine $(\partial H/\partial G)_T$ for the gas.

15. Consider a gas that obeys the equation of state

$$P = \frac{nRT}{V - nb}$$

where b is a constant. Derive an expression for $(\partial U/\partial A)_T$ for the gas.

16. A certain gas obeys the equation of state

$$P = \frac{nRT}{V - nb}$$

where b is a constant. Determine $(\partial U/\partial G)_T$ for the gas.