Chemistry 431
Problem Set 7
Fall 2023
Solutions

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

$$G = A + PV$$
$$= U - TS + PV$$
$$= H - TS$$

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;
   Answer:

$$q_m = \Delta_{r,m}H^{\ominus} = [2(-285.8) + (-393.5) - (-74.6)]\ \text{kJ mol}^{-1} = -890.5\ \text{kJ mol}^{-1}$$

   (b) The maximum amount of work obtainable from the reaction per mole;
   Answer:

$$\Delta_{r,m}G^{\ominus} = [2(-237.1) + (-394.4) - (-50.5)]\ \text{kJ mol}^{-1} = -818.1\ \text{kJ mol}^{-1}$$

$$\Delta_{r,m}A^{\ominus} = \Delta_{r,m}G^{\ominus} - \Delta(PV)$$
$$\Delta_{r,m}A^{\ominus} = \Delta_{r,m}G^{\ominus} - RT\Delta n_{gas}$$
$$= -818100\text{J mol}^{-1} - (8.3144\ \text{J mol}^{-1}\text{K}^{-1})(298\text{K})(-2)$$
$$= -813.1\ \text{kJ mol}^{-1} = \text{maximum total work}$$

   (c) The maximum amount of non-PV work obtainable from the reaction per mole.
   Answer:

$$\text{maximum non} - PV\ \text{work} = \Delta_{r,m}G^{\ominus} = -818.1\ \text{kJ mol}^{-1}$$

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."

Answer:

$$\Delta T = 0 \qquad \text{so that} \qquad \Delta U = \Delta H = 0$$

(a)

$$\text{inital conditions}: \quad P = 1 \text{ bar} \quad T = 298 \text{ K} \quad V = 74.33 \text{ L}$$

(b)

$$\text{after step "a"}: T = 298 \text{ K} \quad V = 148.65 \text{ L} \quad P = 0.50 \text{ bar}$$

(c)

$$\text{after step "b"}: T = 373 \text{ K} \quad V = 148.65 \text{ Ll} \quad P = 0.63 \text{ bar}$$

(d) after step "c":

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$(373 \text{ K})(148.65)^{2/5} = T(73.33)^{2/5}$$

$$T = 495 \text{ K}$$

$$V = 73.33 \text{ L} \quad P = 1.68 \text{ bar}$$

(e)

$$\text{final state}: P = 1.68 \text{ bar} \quad T = 298 \text{ K} \quad V = 44.24 \text{ L}$$

Overall

$$\Delta S = nR \ln \frac{V_f}{V_i} = (3 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{44.24}{73.33} = -12.60 \text{ J K}^{-1}$$

$$\Delta A = \Delta U - T\Delta S = -T\Delta S = \Delta G = -298 \text{ K}(-12.60 \text{ J K}^{-1}) = 3756 \text{ J}$$

$$q_a = 0$$

$$q_b = \frac{5}{2}(3 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(75 \text{ K}) = 4677 \text{ J}$$

$$q_c = 0$$

$$q_d = \frac{7}{2}(3 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K} - 495 \text{ K}) = -17198 \text{ J}$$

$$q = q_a + q_b + q_c + q_d = -12521 \text{ J}$$

$$w = -q = 12521 \text{ J}$$

$$\int \frac{đq_a}{T} = 0$$

$$\int \frac{đq_b}{T} = \int_{298}^{373} \frac{C_V dT}{T}$$

$$= \frac{5}{2}(3 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{373}{298} = 14. \text{ J K}^{-1}$$

$$\int \frac{đq_c}{T} = 0$$

$$\int \frac{đq_d}{T} = C_P \ln \frac{T_f}{T_i}$$

$$= \frac{7}{2}(3 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{298}{495} = -44.30 \text{ J K}^{-1}$$

$$\int \frac{đq}{T} = \int \frac{đq_a}{T} + \int \frac{đq_b}{T} + \int \frac{đq_c}{T} + \int \frac{đq_d}{T} = -30.30 \text{ J K}^{-1}$$

Notice that $\Delta S > \int \frac{đq}{T}$ as it must.

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.
Answer:

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$$

$$dG = -SdT + VdP$$

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

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

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

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

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\frac{nR}{P} - P\left(-\frac{nRT}{P^2}\right) = 0$$

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.

Answer:

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial S}\right)_T = T - P\left(\frac{\partial V}{\partial S}\right)_T$$

$$dA = -SdT - PdV \qquad \left(\frac{\partial V}{\partial S}\right)_T = \left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{\partial U}{\partial S}\right)_T = T - P\left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V - nb} \qquad \text{or} \qquad \left(\frac{\partial T}{\partial P}\right)_V = \frac{V - nb}{nR}$$

$$\left(\frac{\partial U}{\partial S}\right)_T = T - \frac{P(V - nb)}{nR} = \frac{P(V - nb)}{nR} + \frac{an^2}{V^2}\frac{V - nb}{nR} - \frac{P(V - nb)}{nR}$$

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

6. Show that

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

Answer:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P$$

But

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$dG = -SdT + VdP$$

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

Then

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

and

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

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

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

7. For an ideal gas, show that

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

where $\gamma = C_P/C_V$.

Answer:

Simple Solution: For an ideal gas along an adiabatic reversible path

$$PV^\gamma = \text{constant}$$

or

$$P = \frac{\text{constant}}{V^\gamma} \qquad \text{(constant S)}$$

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma(\text{constant})V^{-\gamma-1}$$

$$= -\frac{\gamma P V^\gamma}{V^{\gamma+1}}$$

$$= -\gamma\frac{P}{V}$$

Long Solution:

$$dH = TdS + Vdp$$

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

For an ideal gas

$$dH = C_P dT$$

so that

$$\left(\frac{\partial H}{\partial V}\right)_S = C_P\left(\frac{\partial T}{\partial V}\right)_S$$

or

$$\left(\frac{\partial P}{\partial V}\right)_S = \frac{C_P}{V}\left(\frac{\partial T}{\partial V}\right)_S$$

But

$$\left(\frac{\partial T}{\partial V}\right)_S\left(\frac{\partial V}{\partial S}\right)_T\left(\frac{\partial S}{\partial T}\right)_V = -1$$

so that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V}$$

Now

$$dA = -SdT - PdV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

For an ideal gas

$$dS = \frac{C_V dT}{T} \qquad \text{constant} V$$

so that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

Then

$$\left(\frac{\partial T}{\partial V}\right)_S = -T\frac{(\partial P/\partial T)_V}{C_V}$$

and

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{C_P}{V}\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V$$

But for an ideal gas

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

and

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

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.
Answer:

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial S}\right)_T = T + V\left(\frac{\partial P}{\partial S}\right)_T$$

$$dG = -SdT + VdP$$

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

$$\left(\frac{\partial H}{\partial S}\right)_T = T - V\left(\frac{\partial T}{\partial V}\right)_P$$

$$T = \frac{P(V - nb)}{nR} \qquad \left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{nR}$$

$$\left(\frac{\partial H}{\partial S}\right)_T = T - V\frac{P}{nR} = \frac{PV}{nR} - \frac{Pb}{R} - \frac{PV}{nR} = -\frac{Pb}{R}$$

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

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

   Answer:

   $$dU = TdS + Fd\ell$$

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

   As usual define $A = U - TS$. Then

   $$dA = -SdT + Fd\ell$$

   and

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

   so 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

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

Answer:

$$F = \gamma T \qquad \text{(constant } \ell\text{)}$$

$$\left(\frac{\partial F}{\partial T}\right)_\ell = \gamma$$

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

(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.

Answer:

Define

$$\overline{G} = A - F\ell$$

$$d\overline{G} = dA - Fd\ell - \ell dF$$

$$= -SdT + Fd\ell - Fd\ell - \ell dF$$

$$= -SdT - \ell dF$$

$$\left(\frac{\partial S}{\partial F}\right)_T = \left(\frac{\partial \ell}{\partial T}\right)_F$$

Because

$$\left(\frac{\partial S}{\partial F}\right)_T < 0$$

it follows that

$$\left(\frac{\partial \ell}{\partial T}\right)_F < 0$$

Then if T increases, ℓ decreases and the rubber band contracts. (Try it - Hang a weight at the end of a rubber band to keep F constant, and use a hair dryer to increase the temperature.)

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.

Answer:

$$\left(\frac{\partial U}{\partial \sigma}\right)_T = T\left(\frac{\partial S}{\partial \sigma}\right)_T + \gamma$$

$$A = U - TS$$

$$dA = dU - TdS - SdT = -SdT + \gamma d\sigma$$

$$\left(\frac{\partial S}{\partial \sigma}\right)_T = -\left(\frac{\partial \gamma}{\partial T}\right)_\sigma = -\kappa.$$

Then

$$\left(\frac{\partial U}{\partial \sigma}\right)_T = -\kappa T + \kappa T = 0$$

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.

Answer:

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$dA = -SdT - PdV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial P}{\partial T}\right)_T = \frac{nR}{V-nb} + \frac{an^2}{T^2V^2} \qquad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{(V-nb)^2} + \frac{2an^2}{TV^3}$$

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{nRT}{V-nb} + \frac{an^2}{TV^2} - \frac{nRTV}{(V-nb)^2} + \frac{2an^2}{TV^2}$$

$$= \frac{nRT}{V-nb} + 3\frac{an^2}{TV^2} - \frac{nRTV}{(V-nb)^2}$$

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 $(\partial H/\partial P)_T$.
Answer:

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$dG = -SdT + VdP \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_T$$

$$V = \frac{nRT}{P} + nb \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{nRT}{P} + nb - \frac{nRT}{P} = nb$$

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.
Answer:

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$dA = -SdT - PdV \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb} \qquad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{(V-nb)^2}$$

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{nRT}{V-nb} - \frac{nRT}{V-nb}\frac{V}{V-nb}$$

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.
Answer:

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial G}\right)_T = T\left(\frac{\partial S}{\partial G}\right)_T + V\left(\frac{\partial P}{\partial G}\right)_T$$

$$dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial S}\right)_T = V\left(\frac{\partial P}{\partial S}\right)_T = -V\left(\frac{\partial T}{\partial V}\right)_P$$

$$\left(\frac{\partial S}{\partial G}\right)_T = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial P}{\partial G}\right)_T = \frac{1}{V}$$

$$\left(\frac{\partial H}{\partial G}\right)_T = -\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P + 1$$

$$V = \frac{nRT}{P} + nb \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\left(\frac{\partial H}{\partial G}\right)_T = -\frac{nRT}{PV} + 1 = -1 + \frac{nb}{V} + 1 = \frac{nb}{V}$$

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.
Answer:
Method I

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial A}\right)_T = T\left(\frac{\partial S}{\partial A}\right)_T - P\left(\frac{\partial V}{\partial A}\right)_T$$

$$dA = -SdT - PdV$$

$$\left(\frac{\partial A}{\partial S}\right)_T = -P\left(\frac{\partial V}{\partial S}\right)_T$$

Using an Euler-Maxwell relation

$$\left(\frac{\partial V}{\partial S}\right)_T = \left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{\partial A}{\partial S}\right)_T = -P\left(\frac{\partial T}{\partial P}\right)_V \qquad \left(\frac{\partial S}{\partial A}\right)_T = -\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \qquad \left(\frac{\partial V}{\partial A}\right)_T = -\frac{1}{P}$$

$$\left(\frac{\partial U}{\partial A}\right)_T = -\frac{T}{P}\left(\frac{\partial P}{\partial T}\right)_V + \frac{P}{P}$$

$$-\frac{T}{P}\left(\frac{\partial P}{\partial T}\right)_V = -\frac{nRT}{(V-nb)P} = -1$$

and

$$\left(\frac{\partial U}{\partial A}\right)_T = -1 + 1 = 0$$

Method II

$$dA = -SdT - PdV$$

$$\left(\frac{\partial A}{\partial U}\right)_T = -P\left(\frac{\partial V}{\partial U}\right)_T \qquad \left(\frac{\partial U}{\partial A}\right)_T = -\frac{1}{P}\left(\frac{\partial U}{\partial V}\right)_T$$

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$dA = -SdT - PdV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$= \frac{nRT}{V-nb} - P = 0$$

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.
Answer:

$$dU = TdS - PdV$$

$$dG = -SdT + VdP$$

$$\left(\frac{\partial U}{\partial G}\right)_T = T\left(\frac{\partial S}{\partial G}\right)_T - P\left(\frac{\partial V}{\partial G}\right)_T$$

$$\left(\frac{\partial G}{\partial S}\right)_T = V\left(\frac{\partial P}{\partial S}\right)_T = -V\left(\frac{\partial T}{\partial V}\right)_P$$

$$\left(\frac{\partial S}{\partial G}\right)_T = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial G}{\partial V}\right)_T = V\left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial G}\right)_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial U}{\partial G}\right)_T = -\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P - \frac{P}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$V = \frac{nRT}{P} + nb \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \qquad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$$

$$\left(\frac{\partial U}{\partial G}\right)_T = -\frac{nRT}{PV} + \frac{nRT}{PV} = 0$$