

PHYS 351 #9

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In class we derived the first TdS equation, $TdS = C_V dT + T \frac{\partial P}{\partial T}|_V dV$. Let v be the molar volume and let s be the molar entropy, that is, $v = V/n$ and $s = S/n$. Let c_V be the molar specific heat, $c_V = C_V/n$. Then the first TdS equation can be written for molar specific quantities as $Tds = c_V dT + T \frac{\partial P}{\partial T}|_V dv$.

1.1

The Ideal Gas equation of state is $Pv = RT$. Assume that c_V is constant and integrate the equation of state to show

$$s = s_0 + c_V \ln\left(\frac{T}{T_0}\right) + R \ln\left(\frac{v}{v_0}\right)$$

Note that $\frac{\partial P}{\partial T}|_V = R/v$ so $Tds = c_V dT + T \frac{\partial P}{\partial T}|_V dv$ becomes $ds = c_V/T dT + R/v dv$. We immediately see that if we take the integral we get $s - s_0 = c_V(\ln(T) - \ln(T_0)) + R(\ln(v) - \ln(v_0)) \Rightarrow s = s_0 + c_V \ln\left(\frac{T}{T_0}\right) + R \ln\left(\frac{v}{v_0}\right)$.

1.2

The van der Waals equation of state is $(P + a/v^2)(v - b) = RT$. Assume that c_v is constant and integrate the equation of state to show

$$s = s_0 + c_V \ln(T/T_0) + R \ln\left(\frac{v - b}{v_0 - b}\right)$$

Proceeding in the same fashion. $P = \frac{RT}{(v-b)} - a/v^2$ so $\frac{\partial P}{\partial T}|_V = \frac{R}{(v-b)}$ and $ds = c_V/T dT + \frac{R}{(v-b)} dv$. Integrating both sides and adding s_0 we get $s = s_0 + c_V \ln(T/T_0) + R \ln\left(\frac{v-b}{v_0-b}\right)$.

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Consider one mole of a solid or a liquid under hydrostatic pressure; as above, v is the molar volume.

2.1

Develop an equation of state by expanding dv in terms of dT and dP , and then using the definitions of compressibility and expansion coefficients, β and κ . Show that, if we assume that β and κ are constant, one obtains

$$v = v_0[1 + \beta(T - T_0) - \kappa(P - P_0)]$$

for small changes in v .

We can easily get an expression for v assuming $v(T, P)$ in the usual way $dv = 1/n \frac{\partial V}{\partial T}|_P dT + 1/n \frac{\partial V}{\partial P}|_T dP$. Note using the definitions of κ and β that $dv/v = \beta dT - \kappa dP$. So assuming those two are constant we see $\ln\left(\frac{v-v_0}{v_0} + 1\right) = \beta(T - T_0) - \kappa(P - P_0)$. Noting that $\frac{v-v_0}{v_0}$ is a small quantity (we also must note that it is unit-less) we may use a Taylor expansion on $\ln(x + 1)$ and take the first term x . Thus we get $\frac{v-v_0}{v_0} = \beta(T - T_0) - \kappa(P - P_0)$ or $v = v_0(1 + \beta(T - T_0) - \kappa(P - P_0))$

2.2

In class we derived the second TdS equation, $TdS = C_P dT - T(\frac{\partial V}{\partial T})|P dP$; in terms of molar specific quantities this is $Tds = c_p dT - T(\frac{\partial v}{\partial T})|P dP$. Now use the second TdS equation to find an expression for the change in molar entropy as T and P change. (You should assume that c_p is constant and, as above, that β and κ are constant and that changes in v are small.)

We note that the work from the above section will still be valid here and thus $(\frac{\partial v}{\partial T})|P = v_0 \kappa$. so our equation for entropy becomes $ds = c_p/T dT - v_0 \kappa dP$ and $s = s_0 + \ln(T/T_0) - v_0 \kappa (P - P_0)$.