

11.14: Problems

1. The relationships between H° , S° , and G° for the standard state of a gas and the molar enthalpy, $\bar{H}(P)$, entropy, $\bar{S}(P)$, and Gibbs free energy, $\bar{G}(P)$, of the real gas at pressure P and temperature T involve several integrals. Given the virial equation for a real gas,

$$Z = \frac{P\bar{V}}{RT} = 1 + B^*(T)P + C^*(T)P^2 + D^*(T)P^3 + \dots$$

evaluate the following:

(a)

$$\int_0^P \left[\bar{V} - T \left(\frac{\partial \bar{V}}{\partial T} \right)_P \right] dP$$

(b)

$$\int_0^P \left[\frac{\bar{V}}{RT} - \frac{1}{P} \right] dP$$

(c)

$$\int_{P^*}^P \left(\frac{\partial \bar{V}}{\partial T} \right)_P dP - \int_{P^*}^{1 \text{ bar}} \frac{R}{P} dP$$

2. Why does $(\partial S / \partial P)_{T=0} = -(\partial V / \partial T)_{P, T=0}$ imply that both the entropy and the volume approach their zero-temperature values asymptotically? Is this consistent with defining absolute zero to be the temperature at which the volume of an ideal gas extrapolates to zero—at constant pressure?

3. Prove that

$$\bar{S}_A(P) - S_A^0 = \int_P^{P^*} \left(\frac{\partial \bar{V}}{\partial T} \right)_P dP + \int_{P^*}^{1 \text{ bar}} \frac{R}{P} dP$$

remains finite for any gas in the limit as $P^* \rightarrow 0$. Hint: Express the integral from P to P^* as the sum of integrals from P^* to 1 bar and from 1 bar to P .

4. Let A , B , C , and D be elements, whose absolute entropies at 1 bar and temperature T are $S^\circ(A, T)$, $S^\circ(B, T)$, $S^\circ(C, T)$, and $S^\circ(D, T)$, respectively. Let AB , CD , AC , and BD be binary compounds of these elements, and represent their absolute entropies at these conditions by $S^\circ(AB, T)$, $S^\circ(CD, T)$, $S^\circ(AC, T)$, and $S^\circ(BD, T)$.

(a) What is the entropy change, $\Delta_r S^\circ(T)$, for the reaction $AB + CD \rightarrow AC + BD$?

(b) What are $\Delta_f S^\circ(AB, T)$, $\Delta_f S^\circ(CD, T)$, $\Delta_f S^\circ(AC, T)$, and $\Delta_f S^\circ(BD, T)$?

(c) Show that

$$\Delta_r S^\circ(T) = \Delta_f S^\circ(AC, T) + \Delta_f S^\circ(BD, T) - \Delta_f S^\circ(AB, T) - \Delta_f S^\circ(CD, T)$$

5. Let A and B be elements; let $A_a B_b$ be a binary compound of these elements. At temperature T and 1 bar, let the entropy of these substances be $S^\circ(A, T)$, $S^\circ(B, T)$, and $S^\circ(A_a B_b, T)$, respectively. At absolute zero and 1 bar, let these entropies be $S^\circ(A, 0)$, $S^\circ(B, 0)$, and $S^\circ(A_a B_b, 0)$. Represent the change in entropy when these substances are warmed from 0 K to T , at a constant pressure of 1 bar, as $\Delta_{0 \rightarrow T} S^\circ(A)$, $\Delta_{0 \rightarrow T} S^\circ(B)$, and $\Delta_{0 \rightarrow T} S^\circ(A_a B_b)$. These quantities are related by the following equations:

$$S^\circ(A, T) = S^\circ(A, 0) + \Delta_{0 \rightarrow T} S^\circ(A)$$

$$S^\circ(B, T) = S^\circ(B, 0) + \Delta_{0 \rightarrow T} S^\circ(B)$$

$$S^\circ(A_a B_b, T) = S^\circ(A_a B_b, 0) + \Delta_{0 \rightarrow T} S^\circ(A_a B_b)$$

By the Nernst Heat Theorem, the entropy change for formation of $A_a B_b$ at absolute zero must be zero:

$$\Delta_f S^\circ(A_a B_b, 0) = S^\circ(A_a B_b, 0) - a S^\circ(A, 0) - b S^\circ(B, 0)$$

When, following Planck and Lewis and Randall, we choose to let the entropies of the elements be zero at absolute zero, the entropy of $A_a B_b$ and its entropy of formation also become zero at absolute zero:

$$\Delta_f S^\circ(A_a B_b, 0) = S^\circ(A_a B_b, 0) = 0$$

Suppose that we decide to create an alternative set of absolute entropies by assigning non-zero values to the entropies of the elements at absolute zero. Let us distinguish entropy values in this new scheme with a tilde. Then, the non-zero values that we assign to the elements at absolute zero are $\tilde{S}^\circ(A, 0) \neq 0$ and $\tilde{S}^\circ(B, 0) \neq 0$. By the Nernst Heat Theorem, we have

$$\Delta_f \tilde{S}^\circ(A_a B_b, 0) = \tilde{S}^\circ(A_a B_b, 0) - a \tilde{S}^\circ(A, 0) - b \tilde{S}^\circ(B, 0)$$

Evidently, we have

$$\Delta_f \tilde{S}^\circ(A_a B_b, 0) = \Delta_f S^\circ(A_a B_b, 0) = 0$$

and, since the values of $\tilde{S}^\circ(A, 0)$ and $\tilde{S}^\circ(B, 0)$ are arbitrary, we can choose them so that $\tilde{S}^\circ(A_a B_b, 0)$ is non-zero also

$$\tilde{S}^\circ(A_a B_b, 0) = a \tilde{S}^\circ(A, 0) + b \tilde{S}^\circ(B, 0) \neq 0$$

(a) What are $\tilde{S}^\circ(A, T)$, $\tilde{S}^\circ(B, T)$, and $\tilde{S}^\circ(A_a B_b, T)$?

(b) What is $\Delta_f \tilde{S}^\circ(A_a B_b, T)$?

(c) Show that $\Delta_f \tilde{S}^\circ(A_a B_b, T) = \Delta_f S^\circ(A_a B_b, T)$.

(d) Consider a reaction in which $A_a B_b$ is a reactant or a product. How will the alternative choice of values for the entropies of A and B at absolute zero affect the values we calculate for $\Delta_r S^\circ$, $\Delta_r H^\circ$, $\Delta_r G^\circ$?

(e) Can you think of any circumstance in which there would be an advantage to choosing $\tilde{S}^\circ(A, 0) \neq 0$ and $\tilde{S}^\circ(B, 0) \neq 0$?

6. Find $\ln \gamma$ for a gas that obeys the equation of state $P(\bar{V} - b) = RT$. For CO_2 at 300 K, the value of b (the second virial coefficient) is $-1.26 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$.

Calculate the fugacity coefficient and the fugacity of CO_2 at 300 K and pressures of 1, 10, and 100 bar.

7. Consider the following sequence of steps that convert a van der Waals gas, vdwg, at an arbitrary pressure to the corresponding hypothetical ideal gas in its standard state.

(I) $A(\text{vdwg}, P, T) \xrightarrow{\Delta_I G} A(\text{vdwg}, P^* \approx 0, T)$

(II) $A(\text{vdwg}, P^* \approx 0, T) \xrightarrow{\Delta_{II} G} A(\text{ideal gas}, P^* \approx 0, T)$ (III) $A(\text{ideal gas}, P^* \approx 0, T) \xrightarrow{\Delta_{III} G} A(HIG^\circ, T)$

Show that the fugacity of the van der Waals gas is given by

$$\ln f_{vdw} = \frac{b}{\bar{V} - b} - \frac{2a}{RT\bar{V}} + \ln \frac{RT}{\bar{V} - b}$$

Hint: Find $\Delta G = \Delta_I G + \Delta_{II} G + \Delta_{III} G$. To calculate $\Delta_I G$, use integration by parts:

$$\Delta_I G = \int_P^{P^*} \bar{V}_{vdw} dP = [P\bar{V}]_P^{P^*} - \int_{\bar{V}}^{\bar{V}^*} P d\bar{V}$$

When $P^* \rightarrow 0$, $\bar{V}^* \rightarrow \infty$.

8. The normal boiling point of methanol is 337.8 K at 1 atm. The enthalpy of vaporization at the normal boiling point is $\Delta_{vap} H = 35.21 \text{ kJ mol}^{-1}$.

(a) What are $\Delta_{vap} G$ and $\Delta_{vap} S$ for methanol at its normal boiling point?

(b) At 1 bar, the heat capacity of gaseous methanol depends on temperature as

$$C_P(CH_3OH, g, 1 \text{ bar}) = 21.737 + 0.07494 T \text{ [J K}^{-1} \text{ mol}^{-1}\text{]}$$

Assume that the heat capacity at 1 atm is the same as it is at 1 bar. Calculate the enthalpy change and the entropy change when one mole of gaseous methanol is heated from the normal boiling point to 500 K at 1 atm.

(c) At 1 bar, the absolute entropy of gaseous methanol depends on temperature as

$$S^\circ(CH_3OH, g, 1 \text{ bar}) = 192.8 + 0.1738 T - (5.367 \times 10^{-5}) T^2 \text{ [J K}^{-1} \text{ mol}^{-1}\text{]}$$

Assume that the absolute entropy at 1 atm is the same as it is at 1 bar. Calculate the Gibbs Free Energy change, ΔG , when one mole of gaseous methanol is heated from the normal boiling point to 500 K at a constant pressure of 1 atm.

(d) The heat capacity of liquid methanol,

$$C_P(CH_3OH, \text{liq}, 298.15 \text{ K}, 1 \text{ bar})$$

is $1.1 \text{ J K}^{-1} \text{ mol}^{-1}$. Assume that this heat capacity remains constant for superheated liquid methanol. Calculate the enthalpy and entropy changes when liquid methanol is heated from the normal boiling point to 500 K.

(e) The molar entropy of liquid methanol at 1 bar and 298.15 K is $126.8 \text{ J K}^{-1} \text{ mol}^{-1}$. We can estimate the molar entropy of superheated liquid methanol by using the heat capacity at 298.15 K to estimate the entropy at higher temperatures:

$$S^\circ(T) \approx S^\circ(298.15 \text{ K}) + \int_{298.15}^T \frac{C_P}{T} dT$$

Find $S^\circ(T)$ and use this equation to calculate ΔG for heating liquid methanol from the normal boiling point to 500 K.

(f) Devise a cycle that enables you to use the results you obtain in parts (a)–(e) to calculate $\Delta_{vap}H(500 \text{ K})$, $\Delta_{vap}S(500 \text{ K})$, and $\Delta_{vap}G(500 \text{ K})$ when one mole of methanol vaporizes at 1 atm and 500 K.

(g) Use the values you obtain for $\Delta_{vap}H(500 \text{ K})$ and $\Delta_{vap}S(500 \text{ K})$ in part (f) to calculate $\Delta_{vap}G(500 \text{ K})$.

(h) Use the Gibbs-Helmholtz equation to calculate the Gibbs free energy change, $\Delta_{vap}G(500 \text{ K})$, when one mole of methanol vaporizes at 1 atm and 500 K. Compare this result to those you obtained in parts (f) and (g). Is this process impossible, spontaneous, or reversible?

(i) How much heat is taken up by the system when one mole of methanol is vaporized reversibly at its normal boiling point and the resulting vapor is heated reversibly at 1 atm to 500 K? How much work is done on the system in this process? What are ΔE and ΔS for this process?

(j) Suppose that the change of state in part (i) is effected irreversibly by contacting the liquid methanol with surroundings at 500 K, while maintaining the applied pressure constant at 1 atm. How much work is done on the system in this spontaneous process? How much heat is taken up by the system? What are $\Delta \hat{S}$ and $\Delta S_{universe}$ for this spontaneous process?

9. To maximize the temperature change for a given change in system pressure, the value of $|(\partial T / \partial P)_S|$ should be as large as possible. If only pressure–volume work is possible, we have

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

Show that

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

What happens to T/C_P as the temperature approaches absolute zero? For condensed phases, we find $(\partial V / \partial T)_P \ll V$. Consider the behavior of the molecules in a lattice as the temperature approaches absolute zero. Is it reasonable to expect

$$\lim_{T \rightarrow 0} \left(\frac{\partial V}{\partial T} \right)_P = 0$$

Why?

Notes

¹ Lewis, G.N., Randall, M., K. S. Pitzer, and L. Brewer, *Thermodynamics*, 2nd Edition, McGraw-Hill, New York, 1981, p 130.

² More precisely, we consider a reversible process and a spontaneous process whose initial state is a “change-enabled” modification of the reversible-process initial state. The state functions are the same in both initial states.

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