

10.15: Problems

1. Show that

$$\left(\frac{\partial (A/T)}{\partial T} \right)_V = -\frac{E}{T^2}$$

2. At 60 C, the vapor pressure of water is 19,932 Pa, and the enthalpy of vaporization is 42.482 kJ mol⁻¹.

(a) Is the vaporization of water at these conditions impossible, spontaneous, or reversible? What is ΔG for this process?

(b) Estimate ΔG for the vaporization of liquid water at 19,932 Pa and 70 C. Is this process impossible, spontaneous, or reversible?

(c) Estimate ΔG for the vaporization of liquid water at 19,932 Pa and 50 C. Is this process impossible, spontaneous, or reversible?

3. At 298.15 K and 1 bar, the Gibbs free energy of one mole of N_2O_4 is 4.729 kJ less than the Gibbs free energy of two moles of NO_2 . The enthalpy of one mole of N_2O_4 is 57.111 kJ less than the enthalpy of two moles of NO_2 . We customarily express these facts by saying that the Gibbs free energy and the enthalpy changes for the reaction $2NO_2 \rightarrow N_2O_4$ are $\Delta_r G^\circ(298.15\text{ K}) = -4.729\text{ kJ}$ and $\Delta_r H^\circ(298.15\text{ K}) = -57.111\text{ kJ}$. Assume that the enthalpy change for this process is independent of temperature. Estimate the Gibbs free energy change for this reaction at 500 K and 1 bar, $\Delta_r G^\circ(500\text{ K})$.

4. Over the temperature range $(300\text{ K} \text{ to } 600\text{ K})$, the Gibbs free energy change for the formation of ammonia from the elements, $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$, is well approximated by

$$\Delta_f G^\circ(NH_3) = a + b(T - 600) + c(T - 600)^2 + d(T - 600)^3$$

where $a = 15.824\text{ kJ}$, $b = 0.1120\text{ kJ K}^{-1}$, $c = 1.316 \times 10^{-5}\text{ kJ K}^{-2}$, and $d = -1.324 \times 10^{-8}\text{ kJ K}^{-3}$. Estimate the enthalpy change for this process, $\Delta_f H^\circ(NH_3)$, at 600 K.

5. Consider the total differentials for $S = S(P, T)$, $E = E(P, T)$, $H = H(P, T)$, $A = A(P, T)$, and $G = G(P, T)$. Can we ever encounter an undefined integrand when we evaluate the line integral of one of these total differentials between any two points (P_1, T_1) and (P_2, T_2) ? (In the next chapter, we find that, because of the third law of thermodynamics, no real system can ever reach the absolute zero of temperature.)

6. Consider the total differentials for $S = S(V, T)$, $E = E(V, T)$, $H = H(V, T)$, $A = A(V, T)$, and $G = G(V, T)$. Can we ever encounter an undefined integrand when we evaluate the line integral of one of these total differentials between any two points (V_1, T_1) and (V_2, T_2) ?

7. The normal boiling point of methanol is 337.8 K at 1 atm. The enthalpy of vaporization at the normal boiling point is $\Delta_{vap}H = 35.21\text{ kJ mol}^{-1}$. Is the process impossible, spontaneous, or reversible? Find q , w , $\Delta_{vap}E$, $\Delta_{vap}S$, $\Delta_{vap}A$, $\Delta_{vap}G$ for the vaporization of one mole of methanol at the normal boiling point. Assume that methanol vapor behaves as an ideal gas.

8. For $S = S(P, V)$, we obtain

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

For $S = S(P, T)$, we obtain

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

For temperatures near 4 C and at a pressure of 1 atm, the molar volume of water is given by

$$\bar{V} = \bar{V}_4 + a(T - 277.15)^2$$

where $\bar{V}_4 = 1.801575 \times 10^{-6}\text{ m}^3\text{ mol}^{-1}$ and $a = 1.45 \times 10^{-11}\text{ m}^3\text{ K}^{-1}$. The heat capacity of liquid water is 75.49 J mol⁻¹.

(a) Using $(\partial S/\partial T)_P$, calculate the entropy change when one mole of water is warmed from 2 C to 6 C while the pressure is constant at 1 atm.

(b) Repeat the calculation in (a), for warming the water from 4 C to 6 C.

(c) Can we calculate the entropy change when one mole of water is warmed from 2 C to 6 C using $(\partial S/\partial V)_P$? Why, or why not? The required integral can be transformed to

$$\int \frac{A du}{u^{1/2} + Bu} = \left(\frac{2A}{B} \right) \ln(1 + \beta u^{1/2}) + C$$

where C is an arbitrary constant.

(d) Using $(\partial S/\partial V)_P$, calculate the entropy change when one mole of water is warmed from 4 C to 6 C. Compare this result to the value obtained in (b).

9. For an ideal gas, show that $(\partial E/\partial V)_T$, $(\partial E/\partial P)_T$, $(\partial H/\partial V)_T$, $(\partial H/\partial P)_T$, $(\partial C_V/\partial V)_T$, and $(\partial C_P/\partial P)_T$ are all zero.

10. Find $(\partial E/\partial P)_T$ for a gas that obeys the virial equation of state $P[\bar{V} - B(T)] = RT$, in which $B(T)$ is a function of temperature.

11. Derive the following relationships for an ideal gas:

(a) $dE = C_V dT$

(b) $dS = (C_V/T) dT + (R/V) dV$

(c) $dS = (C_P/T) dT - (R/P) dP$

12. Derive the following relationships for a gas that obeys the virial equation, $P[\bar{V} - B(T)] = RT$, where $B(T)$ is a function of temperature:

(a)

$$d\bar{E} = C_V dT - \left[\frac{RT}{\bar{V} - B} + \frac{RT}{\bar{V} - B} \left(\frac{dB}{dT} \right) - \frac{RT^2}{(\bar{V} - B)^2} \left(\frac{dB}{dT} \right) \right] d\bar{V}$$

(b)

$$d\bar{E} = \left[C_P - R - P \left(\frac{dB}{dT} \right) \right] dT - T \left(\frac{dB}{dT} \right) dP$$

(c)

$$d\bar{S} = \frac{C_V}{T} dT + \left[\frac{R}{\bar{V} - B} + \frac{RT}{(\bar{V} - B)^2} \left(\frac{dB}{dT} \right) \right] d\bar{V}$$

(d)

$$d\bar{S} = \frac{C_P}{T} dT - \left[\frac{R}{P} + \left(\frac{dB}{dT} \right) \right] dP$$

13. One mole of a monatomic ideal gas ($C_V = 3R/2$), originally at 10 bar and 300 K (state A), undergoes an adiabatic free expansion against a constant applied pressure of 1 bar to reach state B. Thereafter the gas is warmed reversibly at constant volume back to 300 K, reaching state C. Finally, the warmed gas is compressed reversibly and isothermally to the original pressure. What are the temperature and volume in state B, following the original adiabatic free expansion? Find q , w , ΔE , ΔH , and ΔS for each of the steps and for the cycle $A \rightarrow B \rightarrow C \rightarrow A$.

14. As in problem 13, one mole of a monatomic ideal gas ($C_V = 3R/2$), originally at 10 bar and 300 K (state A), undergoes an adiabatic free expansion against a constant applied pressure of 1 bar to reach state B. The gas is then returned to its original state in a different two-step process. From state A a reversible constant-pressure warming takes the gas to state D at the original temperature of 300 K. The gas is then returned to state A by an isothermal compression to the original volume. What are the

temperature and volume after the constant-pressure warming step? Find q , w , ΔE , ΔH , and ΔS for each of the steps and for the cycle $A \rightarrow B \rightarrow D \rightarrow A$.

15. As in problem 13, one mole of a monatomic ideal gas ($C_V = 3R/2$), originally at 10 bar and 300 K (state A), undergoes an adiabatic free expansion against a constant applied pressure of 1 bar to reach state B. Now consider a reversible adiabatic expansion from the same initial state, A, that reaches the same temperature as the gas in state B. Call this state F. Find q , w , ΔE , ΔH , and ΔS for the step $A \rightarrow F$. Find q , w , ΔE , ΔH , and ΔS for reversible isothermal expansion from state F to state B. What are q , w , ΔE , ΔH , ΔS , and $\Delta \hat{S}$ for the cycle $A \rightarrow F \rightarrow B \rightarrow A$. Does this cycle violate the machine-based statement of the second law?

16. One mole of carbon dioxide, originally at 10 bar and 300 K, is taken around the cycle in problem 13. Find the energy and entropy changes for the steps in this cycle using the ideal gas equation and the temperature-dependent heat capacity. The constant-volume heat capacity is $C_V = 14.7 + 0.046 \times T$. Find q , w , ΔE , ΔH , and ΔS for each of the steps and for the cycle when CO_2 is taken around the cycle $A \rightarrow B \rightarrow C \rightarrow A$.

17. Ten moles of a monatomic ideal gas, initially occupying a volume of 30 L at 25 C, is expanded against a constant applied pressure of 2 bar. The final temperature is 25 C.

(a) What is the initial pressure? The final volume?

(b) Is this process impossible, spontaneous, or reversible?

(c) Find q , w , ΔE , ΔH , ΔA , ΔS , and ΔG for this process.

18. One mole of CO_2 , originally at 1.00 bar and 300 K, expands adiabatically against a constant applied pressure of 0.200 bar. Assume that CO_2 behaves as an ideal gas with constant heat capacity, $C_V = 28.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

(a) For the spontaneous expansion, we have $dE = C_V dT - P_{\text{applied}} dV$. Find the final temperature and volume for this spontaneous expansion. What is ΔE for this process?

(b) Find the volume and pressure after the gas is compressed adiabatically and reversibly to the original temperature of 300 K. What are ΔS and ΔE for this step?

(c) Find ΔE when the gas in the final state of part (b) is compressed isothermally to the original volume. What is ΔS for this step?

(d) What are ΔE and ΔS for the cycle comprised of the spontaneous expansion of part (a), the adiabatic compression of part (b), and the isothermal compression of part (c)?

(e) What are ΔS , $\Delta \hat{S}$, and $\Delta S_{\text{universe}}$ for the spontaneous expansion?

19. Consider the energy surface depicted in Figure 1. As sketched, E increases monotonically as S increases. E decreases monotonically as V increases. Could the energy surface decrease as S increases or increase as V increases?

20. At 298.15 K, the vapor pressure of water is $3.169 \times 10^{-3} \text{ Pa}$. Some thermodynamic properties for liquid and gaseous water at this temperature and pressure are given in the table below.

	liquid	gas
\bar{G} , kJ mol^{-1}	-237.1	-237.1
\bar{S} , $\text{J mol}^{-1} \text{ K}^{-1}$	70.0	217.5
\bar{E} , kJ mol^{-1}	-285.5	-245.1
C_P , $\text{J mol}^{-1} \text{ K}^{-1}$	75.3	33.6
C_V , $\text{J mol}^{-1} \text{ K}^{-1}$	67.0	25.3

1. Find $\Delta_{\text{vap}} \bar{G}$, $\Delta_{\text{vap}} \bar{S}$, $\Delta_{\text{vap}} \bar{E}$ for water at this temperature and pressure. Is this process reversible, spontaneous, or impossible?

(b) Sketch $\bar{G}(\ell)$ and $\bar{G}(g)$ vs. T for $T(288.15)$. What path is followed when one mole of water at 288.15 K and $3.169 \times 10^3 \text{ Pa}$ goes reversibly to 308.15 K at the same pressure?

(c) On the graph of part (b), indicate the transition in which superheated liquid water at 300 K and 3.169×10^3 Pa goes to gaseous water at 300 K and the same pressure. Is this process spontaneous, reversible, or impossible? Is $\Delta \bar{G}$ for this process positive, zero, or negative?

(d) Sketch $\bar{E}(\ell)$ and $\bar{E}(g)$ vs. T for $T \geq 288.15$. What path is followed when one mole of water at 288.15 K and 3.169×10^3 Pa goes reversibly to 308.15 K at the same pressure?

(e) On the graph of part (b), indicate the transition in which superheated liquid water at 300 K and 3.169×10^3 Pa goes to gaseous water at 300 K and the same pressure. Is $\Delta \bar{E}$ for this process positive, zero, or negative?

21. At 273.15 K and 1 bar, the enthalpy of fusion of ice is 6010 J mol^{-1} . Estimate the Gibbs free energy change for the fusion of ice at 283.15 K and 1 bar.

Notes

¹ J. R. Roebuck and H. Osterberg, *The Joule-Thomson Effect in Nitrogen*, *Phys. Rev.*, Vol. 48, pp 450-457 (1935).

² See T. L. Hill, *An Introduction to Statistical Thermodynamics*, Addison-Wesley Publishing Co., Reading, MA, 1960, pp 266-268.

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