Thermodynamics: Examples for chapter 4.

1. One mole of nitrogen gas is allowed to expand from 0.5 to 10 L (reversible and isothermal process at 300 K). Calculate the change in molar entropy using (a) the ideal gas law and (b) the van der Waals equation with $a = 1.408$ atm L^2 mol^{-2}, $b = 0.03913$ L mol^{-1}.

   Solution:

   a) Use the following equation from the lecture notes:

$$\Delta\bar{S} = nR\ln\left(\frac{V_2}{V_1}\right) = \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right) \times \ln\left(\frac{10 \text{ L}}{0.5 \text{ L}}\right)$$

$$= 24.91 \text{ J K}^{-1} \text{ mol}^{-1}$$

   b) Start with the following equation (see lecture notes):

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

   The equation of state gives:

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

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V - nb} \Rightarrow \Delta S = \int_{V_1}^{V_2} \frac{nR}{V - nb} dV = nR\ln\left(\frac{V_2 - nb}{V_1 - nb}\right)$$

$$\text{or } \Delta\bar{S} = R\ln\left(\frac{\bar{V}_2 - b}{\bar{V}_1 - b}\right)$$

   Plugging in the numerical values gives:

$$\Delta\bar{S} = \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right) \times$$

$$\ln\left(\frac{10 \text{ L} - (1 \text{ mol}) \times (0.03913 \text{ L mol}^{-1})}{0.5 \text{ mol} - (1 \text{ mol}) \times (0.03913 \text{ L mol}^{-1}}\right) = 25.55 \text{ J K}^{-1} \text{ mol}^{-1}$$

2. Derive the relation for $\bar{C}_P - \bar{C}_V$ for a gas that follows the van der Waals equation.

   Solution:

   Based on the lecture notes we have:

$$\bar{C}_P - \bar{C}_V = \frac{T\bar{V}\alpha^2}{\kappa} \text{ with } \alpha = \frac{1}{\bar{V}}\left(\frac{\partial \bar{V}}{\partial T}\right)_P \text{ and } \kappa = -\frac{1}{\bar{V}}\left(\frac{\partial \bar{V}}{\partial P}\right)_T$$

   And the van der Waals equation can be written in the following forms:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \text{ or } T = \frac{1}{R}\left(P\bar{V} - Pb + \frac{a}{\bar{V}} - \frac{ab}{\bar{V}^2}\right)$$

   Next α and κ must be calculated. Since the van der Waals equation of state cannot be written for the molar volume easily, one must use the reciprocal identity:

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{1}{\left(\partial T/\partial \bar{V}\right)_P}$$

$$\alpha^{-1} = \bar{V}\left(\frac{\partial T}{\partial \bar{V}}\right)_P = \bar{V}\left(\frac{P}{R} - \frac{a}{R\bar{V}^2} + \frac{2ab}{R\bar{V}^3}\right) = \left(\frac{P\bar{V}}{R} - \frac{a}{R\bar{V}} + \frac{2ab}{R\bar{V}^2}\right)$$

   It is convenient to eliminate pressure P from this equation by using the van der Waals equation:

$$\alpha^{-1} = \frac{\bar{V}T}{\bar{V} - b} - \frac{2a}{R\bar{V}} + \frac{2ab}{R\bar{V}^2} = \frac{\bar{V}T}{\bar{V} - b} - \frac{2a}{R\bar{V}^2}\left(\bar{V} - b\right)$$

$$\Rightarrow \alpha = \frac{1}{\frac{\bar{V}T}{\bar{V}-b} - \frac{2a}{R\bar{V}^2}\left(\bar{V} - b\right)}$$

   Next we calculate κ:

$$\kappa^{-1} = -\bar{V}\left(\frac{\partial P}{\partial \bar{V}}\right)_T = \frac{\bar{V}RT}{\left(\bar{V}-b\right)^2} - \frac{2a}{\bar{V}^2}$$

Plugging both α and κ into the expression for $\bar{C}_P - \bar{C}_V$ and simplifying, we get:

$$\bar{C}_P - \bar{C}_V = \frac{R}{1 - \frac{2a}{RT}\frac{\left(\bar{V}-b\right)^2}{\bar{V}^3}}$$

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3. Estimate the change in molar entropy of liquid benzene at 25 °C and atmospheric pressure when the pressure is raised to 1000 bar? The coefficient of thermal expansion α is 1.237×10^{-3} K^{-1}, the density is 0.879 g cm^{-3}, and the molar mass is 78.11 g mol^{-1}.

   Solution:

   Based on the lecture notes we have:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = \bar{V}\alpha \Rightarrow \Delta S \approx -\bar{V}\alpha\Delta P$$

   Inserting the values into this equation we get:

$$\Delta\bar{S} \approx -\frac{78.11 \text{ g mol}^{-1}}{0.879 \text{ g cm}^{-3}}\left(10^{-2} \text{ m cm}^{-1}\right)^3\left(1.237 \times 10^{-3} \text{ K}^{-1}\right)\left(999 \times 10^5 \text{ Pa}\right)$$

$$= -10.99 \text{ J K}^{-1} \text{ mol}^{-1}$$

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4. Derive the expression for $(\partial U/\partial V)_T$ (the internal pressure) for a gas following the virial equation with $Z = 1 + B/V$. Consider only PV-work and a reversible process. Note that $B = B(T)$ (i.e. it depends on temperature).

   Solution:

Recall the first law of thermodynamics: $dU = dq + dw$. For PV-work $dw = -PdV$ and by the second law: $dq = TdS$. Thus: $dU = TdS - PdV$ and dividing both sides by dV and imposing constant temperature:

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

The equation of state gives:

$$\frac{P\bar{V}}{RT} = 1 + \frac{B}{V} \Rightarrow P = \frac{RT}{\bar{V}} + \frac{BRT}{\bar{V}^2}$$

Furthermore, differentiation of P with respect to T gives:

$$\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} = \frac{R}{\bar{V}} + \frac{BR}{\bar{V}^2} + \left(\frac{\partial B}{\partial T}\right)\frac{RT}{\bar{V}^2}$$

By inserting these results into the expression derived above:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{\bar{V}} + \frac{BR}{\bar{V}^2} + \left(\frac{\partial B}{\partial T}\right)_{\bar{V}}\frac{RT}{\bar{V}^2}\right) - \frac{RT}{\bar{V}} - \frac{BRT}{\bar{V}^2} = \left(\frac{\partial B}{\partial T}\right)_{\bar{V}}\frac{RT^2}{\bar{V}^2}$$

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5. Consider the process of freezing water at -10 °C for which the enthalpy change is -5619 J mol^{-1} and entropy change is -20.54 J K^{-1} mol^{-1}. What is the Gibbs energy of freezing water at constant temperature of -10 °C?

   Solution:

   The Gibbs energy can be written in terms of enthalpy: $G = H - TS$. At constant temperature we have: $\Delta G = \Delta H - T\Delta S = -5619$ J mol^{-1} $-$ (263.15 K)(-20.54 J K^{-1} mol^{-1}) $= -213.9$ J mol^{-1}.

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6. (a) Integrate the Gibbs-Helmholtz to obtain an expression for ΔG_2 at temperature T_2 in terms of ΔG_1 at T_1, assuming that ΔH is independent of temperature. (b) Obtain an expression for ΔG_2 using a more accurate approximation that $\Delta H = \Delta H_1 + (T - T_1)\Delta C_P$, where T_1 is an arbitrary reference temperature. Assume that ΔC_P is temperature independent. Hint: Integrate one side with respect to variable $\Delta G/T$ and the other with respect to T.

   Solution:

   a) Integrate both sides of the Gibbs-Helmholtz equation (see lecture notes):

$$-\frac{\Delta H}{T^2} = \frac{\partial(\Delta G/T)}{\partial T} \Rightarrow -\int_{T_1}^{T_2} \frac{\Delta H}{T^2} dT = \int_{\Delta G_1/T_1}^{\Delta G_2/T_2} d\left(\Delta G/T\right)$$

$$\Rightarrow \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \Delta G_2/T_2 - \Delta G_1/T_1$$

$$\Rightarrow \Delta G_2 = \Delta H \left(\frac{T_2}{T_2} - \frac{T_2}{T_1}\right) + \Delta G_1 T_2/T_1$$

   b) Assume temperature dependency for $\Delta H(T) = \Delta H_1 + (T - T_1)\,\Delta C_P$:

$$\int_{\Delta G_1/T_1}^{\Delta G_2/T_2} d\left(\Delta G/T\right) = -\int_{T_1}^{T_2} \frac{\Delta H_1}{T^2} dT - \Delta C_P \int_{T_1}^{T_2} \frac{T - T_1}{T^2} dT$$

$$\Rightarrow \frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H_1 \left(\frac{1}{T_2} - \frac{1}{T_1}\right) - \Delta C_P \ln\left(\frac{T_2}{T_1}\right) - \Delta C_P T_1 \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Rightarrow \Delta G_2 = \frac{\Delta G_1 T_2}{T_1} + \Delta H_1 \left(1 - \frac{T_2}{T_1}\right) - \Delta C_P \left(T_2 \ln\left(\frac{T_2}{T_1}\right) + T_1 - T_2\right)$$

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7. An ideal gas is allowed to expand reversibly and isothermally (25 °C) from a pressure of 1 bar to a pressure of 0.1 bar. (a) What is the change in molar Gibbs energy? (b) What would be the change in molar Gibbs energy if the process occurred irreversibly?

   Solution:

   a) Use the following equation (see lecture notes):

$$\Delta G_2 = RT \ln\left(\frac{P_2}{P_1}\right) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times \ln\left(\frac{0.1 \text{ bar}}{1 \text{ bar}}\right)$$

$$= -5.708 \text{ kJ mol}^{-1}$$

   b) Gibbs energy is a state function and depends only on the end-points. Thus the answer is the same as in a).

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8. Helium is compressed isothermally and reversibly at 100 °C from a pressure of 2 to 10 bar. Calculate (a) q per mole, (b) w per mole, (c) $\Delta\bar{G}$, (d) $\Delta\bar{A}$, (e) $\Delta\bar{H}$, (f) $\Delta\bar{U}$, (g) $\Delta\bar{S}$, assuming that helium is an ideal gas.

   Solution:

a) and b) Ideal gas: $\Delta U = 0$ and $q = -w$. The integrated PV-work is:

$$w = RT \ln\left(\frac{P_2}{P_1}\right) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373.15 \text{ K}) \ln\left(\frac{10 \text{ bar}}{2 \text{ bar}}\right)$$

$$= 4993 \text{ J mol}^{-1} \text{ and hence } q = -4993 \text{ J mol}^{-1}$$

   c) The following equation in the lecture notes yields:

$$\Delta\bar{G} = RT \ln\left(\frac{P_2}{P_1}\right) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K}) \ln\left(\frac{10 \text{ bar}}{2 \text{ bar}}\right)$$

$$= 4993 \text{ J mol}^{-1}$$

d) $A = U - TS$ and at constant T: $\Delta A = \Delta U - T\Delta S$. $\Delta U = 0$ and $\Delta A = -T\Delta S$. Also by definition: $\Delta G = \Delta U + \Delta(PV) - T\Delta S = \Delta U - T\Delta S = -T\Delta S$. So $\Delta \bar{G} = \Delta \bar{A}$ in this case and $\Delta \bar{A} = 4993$ J mol^{-1}.

e) $\Delta H = \Delta U + \Delta(PV) = \Delta U = 0$.

f) As already stated $\Delta U = 0$.

g) $\Delta \bar{S} = -\Delta G/T = -13.38$ J K^{-1} mol^{-1}.

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9. Toluene (molecular weight 92.13 g mol^{-1}) is vaporized at constant external pressure and its boiling point, 111 °C (constant temperature). The heat of vaporization at this temperature is 361.9 J g^{-1}. For the vaporization of toluene, calculate (a) w per mole, (b) q per mole, (c) $\Delta \bar{H}$, (d) $\Delta \bar{U}$, (e) $\Delta \bar{G}$, and (f) $\Delta \bar{S}$. In part (a) assume that the volume of the liquid is negligible and that toluene vapor behaves according to the ideal gas law (this assumption is not needed elsewhere). Note also that evaporation at the boiling point is a reversible process.

   Solution:

   a) $w = -P\Delta V = -P(V_{fin} - V_{init}) = -(RT - 0) = -(8.314$ J K^{-1} mol^{-1}) $\times(384$ K$) = -3193$ J mol^{-1}. The final volume was obtained from the ideal gas law ($PV = nRT$).

b) and c) For vaporization process we have $q = \Delta \bar{H} = (361.9$ J g$^{-1}) \times$ (92.13 g mol$^{-1}) = 33.340$ kJ mol^{-1}.

   d) $\Delta \bar{U} = q + w = (33340$ J mol$^{-1}) + (-3193$ J mol$^{-1}) = 30.147$ kJ mol^{-1}. Note that if ideal gas behavior was assumed here, ΔU would have been zero as it would depend only on temperature.

e) and f) $G = U + PV - TS$ and hence $\Delta G = \Delta U + V\Delta P + P\Delta V - T\Delta S - S\Delta T$. At constant temperature and pressure $\Delta P = \Delta T = 0$ and therefore $\Delta G = \Delta U + P\Delta V - T\Delta S$. From part a) $P\Delta V =$ 3193 J mol^{-1} and we need to calculate ΔS. $\Delta S = q_{rev}/T =$ (33.340 kJ mol^{-1})/(384 K) = 86.8 J K^{-1} mol^{-1}. And finally $\Delta G =$ 0 by combining all the required terms.

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10. Calculate $\Delta_{mix}G$ and $\Delta_{mix}S$ for the formation of a quantity of air containing 1 mol of gas by mixing nitrogen and oxygen at 298.15 K. Air may be taken to be 80% nitrogen and 20% oxygen (in mol %). Assume ideal gas behavior.

    Solution:

    In the lecture notes, the following realtions were given:

$$\Delta_{mix}G = RT\left(n_1 \ln(y_1) + n_2 \ln(y_2)\right)$$
$$\Delta_{mix}S = -R\left(n_1 \ln(y_1) + n_2 \ln(y_2)\right)$$
$$\Delta_{mix}H = \Delta_{mix}V = 0$$

    $n_1 = 0.80$ mol of N_2 ($y_1 = 0.80$) and $n_2 = 0.20$ mol of O_2 ($y_2 = 0.20$). By inserting the values in above equations, we get: $\Delta_{mix}G = -1239$ J mol^{-1} and $\Delta_{mix}S = 4.159$ J K^{-1} mol^{-1}.