10.40 Thermodynamics   **Fall 2003**
Problem Set 11

Problem 17.9 Text

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Problem 17.9 in the texbook. Please note that some printings of the book have a typo in Figure P17.9. Specifically, the labels on the univariant loci for the H-$H_2O_{(l)}$-$CO_{2(g)}$ and H-$H_2O_{(s)}$-$CO_{2(g)}$ curves are reversed in some printings.

Figure removed. Please see "Tester, J. W., and Michael Modell. *Thermodynamics and Its Applications*. Upper Saddle River, NJ: Prentice Hall PTR, 1997, p. 857. Fig. P17.9."

Solution:
(a)

The maximum temperature and pressure at which H-$H_2O_{(l)}$-$CO_{2(g)}$ exists is the quadruple point of H-$H_2O_{(l)}$-$CO_{2(g)}$-$CO_{2(l)}$ at 50°F (10°C) and 600 psi (4 MPa).

(b)

There are several different ways that this problem can be solved depending on whether or not the hydrate is considered to be a mixture of water and carbon dioxide or if it is considered a new compound. In addition, methods from Chapter 15 could be used or the same methods in matrix form which are developed in Chapter 17 could be employed.

There are some assumptions that are common to all of the methods.
1. $x_{H_2O}^{L} \approx 1, \quad x_{CO_2}^{V} \approx 1$
2. The vapor phase behavior can be approximated by the ideal gas law

Method I – Hydrate as a mixture, Chapter 15 methods

Assume that hydrate is a separate phase, but it is not a new compound. It is a mixture of water and carbon dioxide in the hydrate phase.

The phase rule shows that the system is monovariant.
$$\mathfrak{I} = n + 2 - \pi - r = 2 + 2 - 3 - 0 = 1$$

Using the differential approach for water:

$$d \ln \hat{f}^H_{H_2O} = d \ln f^L_{H_2O}$$

$$-\frac{\bar{H}^H_{H_2O} - H^0_{H_2O}}{RT^2} dT + \frac{\bar{V}^H_{H_2O}}{RT} dP + \left(\frac{\partial \ln \hat{f}^H_{H_2O}}{\partial x^H_{H_2O}} \right)_{T,P} dx^H_{H_2O} = -\frac{H^L_{H_2O} - H^0_{H_2O}}{RT^2} dT + \frac{V^L_{H_2O}}{RT} dP$$

Combining to yield

$$-\frac{\bar{H}^H_{H_2O} - H^L_{H_2O}}{RT^2} dT + \frac{\bar{V}^H_{H_2O} - V^L_{H_2O}}{RT} dP + \left(\frac{\partial \ln \hat{f}^H_{H_2O}}{\partial x^H_{H_2O}} \right)_{T,P} dx^H_{H_2O} = 0 \tag{1}$$

Similarly for CO_2, equating the fugacity of CO_2 in the vapor and hydrate phases,

$$-\frac{\bar{H}^H_{CO_2} - H^V_{CO_2}}{RT^2} dT + \frac{\bar{V}^H_{CO_2} - V^V_{CO_2}}{RT} dP + \left(\frac{\partial \ln \hat{f}^H_{CO_2}}{\partial x^H_{CO_2}} \right)_{T,P} dx^H_{CO_2} = 0 \tag{2}$$

Multiplying Eq. (1) by $x^H_{H_2O}$ and Eq. (2) by $x^H_{CO_2}$ and applying the Gibbs-Duhem equation:

$$\left(\frac{\partial \ln \hat{f}^H_{H_2O}}{\partial x^H_{H_2O}} \right)_{T,P} x^H_{H_2O} + \left(\frac{\partial \ln \hat{f}^H_{CO_2}}{\partial x^H_{CO_2}} \right)_{T,P} x^H_{CO_2} = 0 \tag{3}$$

Combining Eqs. (1) through (3)

$$-\frac{x^H_{H_2O} \left(\bar{H}^H_{H_2O} - H^L_{H_2O} \right) + x^H_{CO_2} \left(\bar{H}^H_{CO_2} - H^V_{CO_2} \right)}{RT^2} dT + \frac{x^H_{H_2O} \left(\bar{V}^H_{H_2O} - V^L_{H_2O} \right) + x^H_{CO_2} \left(\bar{V}^H_{CO_2} - V^V_{CO_2} \right)}{RT} dP = 0$$

Applying $B = \sum_i x_i \bar{B}_i$

$$-\frac{H^H - \left(x^H_{H_2O} H^L_{H_2O} + x^H_{CO_2} H^V_{CO_2} \right)}{RT^2} dT + \frac{V^H - \left(x^H_{H_2O} V^L_{H_2O} + x^H_{CO_2} V^V_{CO_2} \right)}{RT} dP = 0 \tag{4}$$

Define
$$\Delta H_f \text{ (formation of H)} = H^H - \left(x^H_{H_2O} H^L_{H_2O} + x^H_{CO_2} H^V_{CO_2} \right)$$

Where $x^H_{H_2O} = \frac{23}{27}, \quad x^H_{CO_2} = \frac{3}{27}$

Assuming

$$V_{CO_2}^V \gg V_{H_2O}^L, V^H$$

Eq. (4) simplifies to,

$$\frac{dP}{dT} = -\underbrace{\left(\frac{\Delta H_f}{x_{CO_2}^H}\right)}_{\Delta H^*}\frac{1}{V_{CO_2}^V T} \qquad (5)$$

and assuming ideal gas conditions

$$\frac{dP}{dT} = \frac{-\Delta H^*}{RT^2/P} \qquad \text{which simplifies to}$$

$$\frac{d\ln P}{d(1/T)} \approx \frac{d\ln P}{dT} = \frac{\Delta H^*}{R} \qquad \text{since the problem statement says that } d(1/T) \approx dT$$

Assuming that the enthalpies of the hydrate, liquid, and vapor phases are constant over the temperature and pressure ranges, then ΔH^* is constant.

$$\frac{d\ln P}{dT} = \frac{\Delta H^*}{R} = \text{constant} \qquad (6)$$

So the linear behavior of ln$P$ versus T as shown in Figure P17.9 is reasonable.

Method II – Hydrate as a mixture, Chapter 17 methods

3 phases: V-1, L-2, H-3
2 components: CO_2-1, H_2O-2
0 reactions

Applying Eqs. (17-37) through (17-39)

$$\left.\frac{dP}{dT}\right]_{\Im=1} = \frac{\left|\Delta \underset{\sim}{H}\right|}{T\left|\Delta \underset{\sim}{V}\right|} \qquad (7)$$

Where

$$\left|\Delta \underset{\sim}{H}\right| = \begin{vmatrix} H^V & x_{CO_2}^V & x_{H_2O}^V \\ H^L & x_{CO_2}^L & x_{H_2O}^L \\ H^H & x_{CO_2}^H & x_{H_2O}^H \end{vmatrix} = \begin{vmatrix} H^V & 1 & 0 \\ H^L & 0 & 1 \\ H^H & x_{CO_2}^H & x_{H_2O}^H \end{vmatrix} = -x_{CO_2}^H H^V - x_{H_2O}^H H^L + H^H \qquad (8)$$

$$\left|\Delta\underset{\sim}{V}\right| = \begin{vmatrix} V^V & x^V_{CO_2} & x^V_{H_2O} \\ V^L & x^L_{CO_2} & x^L_{H_2O} \\ V^H & x^H_{CO_2} & x^H_{H_2O} \end{vmatrix} = \begin{vmatrix} V^V & 1 & 0 \\ V^L & 0 & 1 \\ V^H & x^H_{CO_2} & x^H_{H_2O} \end{vmatrix} = -x^H_{CO_2}V^V - x^H_{H_2O}V^L + V^H \tag{9}$$

Define

$$\Delta H_f \text{ (formation of H)} = H^H - \left(x^H_{H_2O}H^L_{H_2O} + x^H_{CO_2}H^V_{CO_2} \right)$$

Where $x^H_{H_2O} = \dfrac{23}{27}, \quad x^H_{CO_2} = \dfrac{4}{27}$

Assuming

$V^V_{CO_2} \square\ V^L_{H_2O}, V^H$ and ideal gas assumptions Eq. (9) simplifies to

$$\frac{dP}{dT} = -\left(\frac{\Delta H_f}{x^H_{CO_2}} \right)\frac{1}{V^V_{CO_2}T} \tag{10}$$

Eq. (10) is the same as Eq. (5). The rest of the solution is the same as Method I.

Method III – Hydrate as a compound, Chapter 17 methods

This method is similar to example 17.2.

3 phases: V-1, L-2, H-3
3 components: CO_2-1, H_2O-2, H-3
1 reaction: $CO_2 + 5\frac{3}{4}H_2O \rightarrow H$
In addition to the assumptions that $x^L_{H_2O} \approx 1$, $x^V_{CO_2} \approx 1$, we also assume that $x^H_H = 1$.

Plugging the mole fractions for this problem into Eq. (17-53) yields

$$\frac{dP}{dT}\bigg]_{\Im=1} = \frac{\begin{vmatrix} H^V & 1 & 0 \\ H^L & 0 & 1 \\ H^H & 1 & v^H_{H_2O} \end{vmatrix}}{T\begin{vmatrix} V^V & 1 & 0 \\ V^L & 0 & 1 \\ V^H & 1 & v^H_{H_2O} \end{vmatrix}} = \frac{-H^V - v^H_{H_2O}H^L + H^H}{T\left(-V^V - v^H_{H_2O}V^L + V^H\right)} \tag{11}$$

$$\Delta H_{rx} = \sum_i v_i H_i = H^H - H^V - v^H_{H_2O}H^L \tag{12}$$

Assuming

$V^V \square V^L, V^H$ and ideal gas assumption, Eq. (11) simplifies to

$$\frac{dP}{dT}\bigg]_{\Im=1} = \frac{-\Delta H_{rx}}{RT^2/P} \tag{13}$$

Simplifying Eq. (13) using a similar approach to method I yields,

$$\frac{d\ln P}{dT} = \frac{\Delta H_{rx}}{R} \tag{14}$$

Assuming that the enthalpies of the hydrate, vapor, and liquid phases are constant over the temperature and pressure range, Eq. (14) is equal to a constant. So the linear behavior of ln$P$ versus T as shown in Figure P17.9 is reasonable.

(c)

For salt (S) addition up to 3.5% wt, assume that salt is only present as a solute in the liquid phase, so $x_S^H = x_S^V = 0$ and $x_S^L + x_{H_2O}^L = 1$. It is simplest to solve this problem by considering the hydrate phase to be a mixture of fixed ratios of water and carbon dioxide, instead of considering the hydrate to be a new compound.

Now that we have an extra component, our phase rule changes from method I, part b to

$$\Im = n + 2 - \pi - r = 3 + 2 - 3 - r = 2 - r$$

To make the problem monovariant, we need to choose another restraint, r. If we choose to hold the concentration of the salt in the water phase constant, then we will end up with a solution very similar to that in part (b), except the value of ΔH_f will be different, resulting in a different slope and intercept of the equilibrium curve. However, this answer does not help us since we do not know the value of ΔH_f. Instead, we want to look at the effect of changing the concentration on the temperature while holding pressure constant. Basically, we want to look at the effect on the freezing point temperature of water (liquid to hydrate phase) as a function of the salt concentration. We can use two different methods to analyze this effect either using Chapter 15 or Chapter 17 methods.
Method I, Chapter 15

We start out the problem in a similar way to Method I, part (a), but now we are holding the pressure constant and allowing the mole fraction of water in the liquid phase to vary.

Using the differential approach for water:

$$d \ln \hat{f}^{H}_{H_2O} = d \ln \hat{f}^{L}_{H_2O}$$

$$-\frac{\bar{H}^{H}_{H_2O} - H^{0}_{H_2O}}{RT^2} dT + \left(\frac{\partial \ln \hat{f}^{H}_{H_2O}}{\partial x^{H}_{H_2O}}\right)_{T,P} dx^{H}_{H_2O} = -\frac{H^{L}_{H_2O} - H^{0}_{H_2O}}{RT^2} dT = \left(\frac{\partial \ln \hat{f}^{L}_{H_2O}}{\partial x^{L}_{H_2O}}\right)_{T,P} dx^{L}_{H_2O}$$

Combining to yield

$$-\frac{\bar{H}^{H}_{H_2O} - H^{L}_{H_2O}}{RT^2} dT + \left(\frac{\partial \ln \hat{f}^{H}_{H_2O}}{\partial x^{H}_{H_2O}}\right)_{T,P} dx^{H}_{H_2O} - \left(\frac{\partial \ln \hat{f}^{L}_{H_2O}}{\partial x^{L}_{H_2O}}\right)_{T,P} dx^{L}_{H_2O} = 0 \qquad (14)$$

The similar equation for carbon dioxide is unchanged and is shown in Eq. (2). Applying the Gibbs-Duhem equation as we did in Method I, part (a) and combining Eqs. (2) and (14),

$$-\frac{x^{H}_{H_2O}\left(\bar{H}^{H}_{H_2O} - \bar{H}^{L}_{H_2O}\right) + x^{H}_{CO_2}\left(\bar{H}^{H}_{CO_2} - H^{V}_{CO_2}\right)}{RT^2} dT - x^{H}_{H_2O}\left(\frac{\partial \ln \hat{f}^{L}_{H_2O}}{\partial x^{L}_{H_2O}}\right)_{T,P} dx^{L}_{H_2O} = 0 \qquad (15)$$

Noting that $H^{H} = x^{H}_{H_2O}\bar{H}^{H}_{H_2O} + x^{H}_{CO_2}\bar{H}^{H}_{CO_2}$ and assuming that the ocean is large enough that $\bar{H}^{L}_{H_2O}$ is constant throughout. Define $\Delta H^{*}_{f} = \left(H^{H} - x^{H}_{H_2O}\bar{H}^{L}_{H_2O} - x^{H}_{CO_2}H^{V}_{CO_2}\right)/x^{H}_{H_2O}$ which is the enthalpy of formation of the hydrate mixture on a per mole of water basis.

In order to evaluate the second term in Eq. (15), we need to assume as fugacity model for water in the liquid phase.

$$\hat{f}^{L}_{H_2O} = \gamma^{L}_{H_2O} x^{L}_{H_2O} f^{+}_{H_2O} \qquad (16)$$

Assuming a pure component reference state for water, so $f^{+}_{H_2O} = f^{L}_{H_2O} = f(T,P)$ only. Since we are only looking at the range of salt = 0 to 3.5wt %, water is almost pure throughout the composition range of interest. Therefore, it is a good approximation to set $\gamma^{L}_{H_2O} = 1$. Eq. (15) simplifies to:

$$-\frac{\Delta H^{*}_{f}}{RT^2} dT - \left(\frac{1}{x^{L}_{H_2O}}\right) dx^{L}_{H_2O} = 0 \qquad (17)$$

Rearranging,

$$\left(\frac{dT}{dx^{L}_{H_2O}}\right)_{P} = \frac{-RT^2}{\Delta H^{*}_{f} x^{L}_{H_2O}} \qquad (18)$$

Assuming that ΔH_f^* is constant over the composition range of interest, Eq. (18) can be integrated,

$$\int_{T^0}^{T} -\frac{\Delta H_f^*}{RT^2}\, dT = \int_{1}^{1-x_S^L} \frac{1}{x_{H_2O}^L}\, dx_{H_2O}^L \qquad (19)$$

$$\frac{\Delta H_f^*}{RT^2}\left(\frac{1}{T} - \frac{1}{T^0}\right) = \ln\left(1 - x_S^L\right) - \underbrace{\ln(1)}_{=0} \qquad (20)$$

Where $\ln\left(1 - x_S^L\right) \approx -x_S^L$ for small x_S^L and $\dfrac{1}{T} - \dfrac{1}{T^0} = \dfrac{T^0 - T}{T^0 T} \approx \dfrac{T^0 - T}{\left(T^0\right)^2}$ for $T \approx T^0$. Eq. (20)

simplifies to:

$$T^0\left(P, x_S^L = 0\right) - T\left(P, x_S^L > 0\right) = \frac{-R\left(T^0\right)^2}{\Delta H_f^*}\, x_S^L \qquad (21)$$

$\Delta H_f^* < 0$ since the enthalpy of the hydrate (a solid phase) is less than the enthalpy of the liquid and vapor phases from which it was formed. So, the left side of Eq. (21) is positive. Since T^0 is greater than T, addition of salt to the water moves the equilibrium line to the left. This behavior is a type of freezing point *depression*.

Method II, Chapter 17

To look at $\dfrac{\partial T}{\partial x_S^L}$, we use the methods developed in Chapter 17, section 5. The methods in this section are only applicable for the non-reacting model since this section assumes that there are no reactions in its derivations. First we number the phases and the components.

3 phases: V-1, L-2, H-3
2 components: H_2O-1, CO_2-2, S-3
0 reactions, hold pressure constant

We start with Eq. (17-71) with the beta phase equal to the liquid phase for our problem. This equation expresses variations in mole fraction of component one. We have chosen water to be the component one instead of salt for reasons that will become clear as we continue this problem. At the end, we will relate variation of water in the liquid phase to variations of salt in the liquid phase by the relation: $x_S^L + x_{H_2O}^L = 1$.

$$\left[\frac{\partial T}{\partial x_{H_2O}^L}\right]_{P,[\mathfrak{I}=1]} = \frac{-RT^2\left|\underset{\sim}{x}_i^{(S)}\right|\left[\frac{\partial \ln \hat{f}_{H_2O}^L}{\partial x_{H_2O}^L}\right]_{T,P}}{\left[\left|\Delta\underset{\sim}{H}^\infty\right| - \bar{H}_{H_2O}^L\left|\underset{\sim}{x}_i^{(S)}\right|\right]} \tag{22}$$

Solving for components of Eq. (22),

$$\left|\Delta\underset{\sim}{H}^\infty\right| = \begin{vmatrix} H^V & x_{CO_2}^V & x_S^V \\ H^L & x_{CO_2}^L & x_S^L \\ H^H & x_{CO_2}^H & x_S^H \end{vmatrix} = \begin{vmatrix} H^V & 1 & 0 \\ H^L & 0 & 1-x_{H_2O}^L \\ H^H & x_{CO_2}^H & 0 \end{vmatrix} = -H^V x_{CO_2}^H\left(1-x_{H_2O}^L\right) + H^H\left(1-x_{H_2O}^L\right) \tag{23}$$

Where $x_{H_2O}^H = \dfrac{23}{27}$, $\quad x_{CO_2}^H = \dfrac{3}{27}$

$$\left|\Delta\underset{\sim}{x}_i^{(S)}\right| = \begin{vmatrix} x_{H_2O}^V & x_{CO_2}^V & x_S^V \\ x_{H_2O}^L & x_{CO_2}^L & x_S^L \\ x_{H_2O}^H & x_{CO_2}^H & x_S^H \end{vmatrix} = \begin{vmatrix} 0 & 1 & 0 \\ x_{H_2O}^L & 0 & 1-x_{H_2O}^L \\ x_{H_2O}^H & x_{CO_2}^H & 0 \end{vmatrix} = x_{H_2O}^H\left(1-x_{H_2O}^L\right) \tag{24}$$

We can use the same fugacity model for water in the liquid phase that we used in Method 1, part (c).

$$\hat{f}_{H_2O}^L = \gamma_{H_2O}^L x_{H_2O}^L f_{H_2O}^+ \tag{16}$$

The reason why we choose water as component one instead of salt is that we have a fugacity model for water which is easy to evaluate. Now we apply Eq. (16) as we did before. Assuming a pure component reference state for water, $f_{H_2O}^+ = f_{H_2O}^L = f(T,P)$ only. Since we are only looking at the range of salt = 0 to 3.5wt %, water is almost pure throughout the composition range of interest. Therefore, it is a good approximation to set $\gamma_{H_2O}^L = 1$.

$$\left[\frac{\partial \ln \hat{f}_{H_2O}^L}{\partial x_{H_2O}^L}\right]_{T,P} = \frac{1}{x_{H_2O}^L} \tag{25}$$

Plugging Eqs. (23) through (25) into Eq. (23) yields

$$\left[\frac{\partial T}{\partial x_{H_2O}^L}\right]_{P,[\mathfrak{I}=1]} = \frac{-RT^2\left(1-x_{H_2O}^L\right)x_{H_2O}^H\left(\dfrac{1}{x_{H_2O}^L}\right)}{H^H\left(1-x_{H_2O}^L\right) - \bar{H}_{H_2O}^L\left(1-x_{H_2O}^L\right)x_{H_2O}^H - H^V x_{CO_2}^H} \tag{26}$$

Canceling out the common factor of $\left(1 - x_{H_2O}^L\right)$ and defining

$\Delta H_f^* = \left(H^H - x_{H_2O}^H \bar{H}_{H_2O}^L - x_{CO_2}^H H_{CO_2}^V\right)/x_{H_2O}^H$ which is the enthalpy of formation of the hydrate mixture on a per mole of water basis, yields

$$\left(\frac{dT}{dx_{H_2O}^L}\right)_P = \frac{-RT^2}{\Delta H_f^* x_{H_2O}^L} \tag{27}$$

Eq. (27) is the same as Eq. (18), which is developed using Method I, part (c). The rest of this solution is the same as Method I, part (c).

(d)

At 1000m the pressure is given by

$$P = \rho g h = \left(1000 kg/m^3\right)\left(9.81 m/s^2\right)\left(1000m\right) = 9.81 MPa \tag{28}$$

At a temperature of 1 to 2°C and a pressure of approximately 9.8 MPa, the phase diagram shows that the stable phases are hydrate and liquid carbon dioxide.

When liquid carbon dioxide is released at the bottom of the ocean, it forms a bubble/pool that sits on the ocean floor. Initially hydrate would form on the surface of the carbon dioxide. There would never be complete conversion of carbon dioxide to hydrate, since at equilibrium there should always be some carbon dioxide present. Water from the ocean would diffuse through the hydrate and into the liquid carbon dioxide in order to form more hydrate. At the same time, liquid carbon dioxide could diffuse through the hydrate out into the ocean where it would be carried away into the nearly infinite ocean. Eventually, enough carbon dioxide would have escaped into the ocean that the hydrate would have to start converting back into carbon dioxide in order to maintain the hydrate-carbon dioxide equilibrium. After a very long time, all of the hydrate would disappear, so liquid carbon dioxide is not stable on the ocean floor. Some of the key unknowns in this problem are:
- Rate of hydrate formation
- Rate of water diffusion through the hydrate
- Rate of carbon dioxide diffusion through the hydrate