REB, The Book
Example 2.6.4 Solution

Suppose a system initially contains 1 mole of CH_4 and 2.5 moles of H_2O. Reactions (1) through (4) occur at 920 °C with 88% conversion of CH_4 and a CO yield of 65%. Selected thermodynamic data are presented in Table 1. Generate the necessary expressions for heats of reaction and use them to calculate the net heat released.

$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \tag{1}$$

$$CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2 \tag{2}$$

$$CH_4 + 2\ H_2O \rightarrow CO_2 + 4\ H_2 \tag{3}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4}$$

Table 1. Ideal gas standard heats of formation (kcal mol–1) and heat capacities (cal mol–1 K–1 for T in K) from Reid, Prausnitz and Sherwood1.

i	$\Delta H_{f,i}\big\|_{T=298K}$	$\hat{C}_{p,i}$
CH_4	–17.89	4.598 + 1.245 x 10^{-2} T + 2.86 x 10^{-6} T^2 – 2.703 x 10^{-9} T^3
H_2O	–57.8	7.701 + 4.595 x 10^{-4} T + 5.521 x 10^{-6} T^2 - 0.859 x 10^{-9} T^3
CO	–26.42	7.373 - 3.07 x 10^{-3} T + 6.662 x 10^{-6} T^2 - 3.037 x 10^{-9} T^3
H_2	0.0	6.483 + 2.215 x 10^{-3} T - 3.298 x 10^{-6} T^2 + 1.826 x 10^{-9} T^3
CO_2	–94.05	4.728 + 1.754 x 10^{-2} T - 1.338 x 10^{-5} T^2 + 4.097 x 10^{-9} T^3

[1] Reid, Robert C., J. M. Prausnitz, and Thomas Kilgore Sherwood, "The Properties of Gases and Liquids." McGraw-Hill, 1977.

The number of independent reactions is equal to the rank of the transpose of the stoichiometric coefficient matrix, equation (5), where the rows correspond to reactions (1) through (4) and the columns, from left to right, to CH_4, H_2O, CO, H_2, and CO_2. The rank of that matrix is 2. A working matrix containing only the first two rows of that matrix also has a rank of 2, so reactions (1) and (2) are a complete, mathematically independent subset of the reactions.

$$\boldsymbol{\nu}^T = \begin{bmatrix} -1 & -1 & 1 & 3 & 0 \\ -1 & 0 & 2 & 2 & -1 \\ -1 & -2 & 0 & 4 & 1 \\ 0 & -1 & -1 & 1 & 1 \end{bmatrix} \tag{5}$$

The net heat released will equal the heats of those two reaction multiplied by their apparent extents. The heats can be found using Table 1 and the extents from the given conversion and yield.

The standard heats of reactions (1) and (2) at 298 K are calculated as shown in equations (6) and (7).

$$\begin{aligned} \Delta H_1\Big|_{T=298K} &= -\,\Delta H_{f,CH_4}\Big|_{T=298K} + -\Delta H_{f,H_2O}\Big|_{T=298K} \\ &\quad + \Delta H_{f,CO}\Big|_{T=298K} + 3\Delta H_{f,H_2}\Big|_{T=298K} \end{aligned} \tag{6}$$

$$\begin{aligned} \Delta H_2\Big|_{T=298K} &= -\,\Delta H_{f,CH_4}\Big|_{T=298K} - \Delta H_{f,CO_2}\Big|_{T=298K} \\ &\quad + 2\Delta H_{f,CO}\Big|_{T=298K} + 2\Delta H_{f,H_2}\Big|_{T=298K} \end{aligned} \tag{7}$$

The standard heat of reaction (1) at any other temperature can be calculated as shown in equation (8). The analogous expression for reaction (2) is shown in equation (9). The heat released is the negative of the heat of reaction.

$$\begin{aligned} \Delta H_1 = \Delta H_1\Big|_{T=298K} &- \int_{289K}^{T} \hat{C}_{p,CH_4} dT - \int_{289K}^{T} \hat{C}_{p,H_2O} dT \\ &+ \int_{289K}^{T} \hat{C}_{p,CO} dT + 3\int_{289K}^{T} \hat{C}_{p,H_2} dT \end{aligned}$$

$$
\begin{aligned}
\Delta H_1 = \Delta H_1\Big|_{T=298K} \\
&- \int_{289K}^{T} \left(4.598 + 1.245x10^{-2}T + 2.86x10^{-6}T^2 - 2.703x10^{-9}T^3\right) dT \\
&- \int_{289K}^{T} \left(7.701 + 4.595x10^{-4}T + 5.521x10^{-6}T^2 - 0.859x10^{-9}T^3\right) dT \\
&+ \int_{289K}^{T} \left(7.373 - 3.07x10^{-3}T + 6.662x10^{-6}T^2 - 3.037x10_{-9}T^3\right) dT \\
&+3 \int_{289K}^{T} \left(6.483 + 2.215x10^{-3}T - 3.298x10^{-6}T^2 + 1.826x10^{-9}T^3\right) dT
\end{aligned}
$$

$$
\begin{aligned}
\Delta H_1 = \Delta H_1\Big|_{T=298K} + 14.523T - 0.0046673T^2 - 3.871 \times 10^{-6}T^3 \\
+1.50075 \times 10^{-9}T^4
\end{aligned}
\qquad (8)
$$

$$
\begin{aligned}
\Delta H_2 = \Delta H_2\Big|_{T=298K} + 18.386T - 0.01585T^2 + 5.916 \times 10^{-6}T^3 \\
-9.54 \times 10^{-10}T^4
\end{aligned}
\qquad (9)
$$

The conversion and the yield can be expressed in terms of the apparent extents of reaction as shown in equations (10) and (11). Using the given initial moles of CH4, CH4 conversion and CO yield, equations (10) and (11) can be solved for the apparent extents of reactions (1) and (2).

$$
f_{CH_4} = \frac{n_{CH_4,0} - n_{CH_4}}{n_{CH_4,0}} = \frac{n_{CH_4,0} - \left(n_{CH_4,0} - \xi_1 - \xi_2\right)}{n_{CH_4,0}} = \frac{\xi_1 + \xi_2}{n_{CH_4,0}} \qquad (10)
$$

$$
Y_{CO/CH_4} = \frac{n_{CO}}{n_{CH_4,0}} = \frac{\cancel{n_{CO,0}} + \xi_1 + 2\xi_2}{n_{CH_4,0}} = \frac{\xi_1 + 2\xi_2}{n_{CH_4,0}} \qquad (11)
$$

The standard heats of reactions (1) and (2) at 920 °C (1193 K) can be calculated using equations (8) and (9). The net heat released, $\dot{Q}_{released}$ is then given by equation (12).

$$\dot{Q}_{released} = -\Delta H_1\Big|_{T=1193K}\xi_1 - \Delta H_2\Big|_{T=1193K}\xi_2 \tag{12}$$

The calculations were performed as described above. The standard heats of reactions (1) and (2) at 920 °C are 52.6 and 62.4 kcal mol^{-1}, respectively. That is, both reactions are endothermic as written, so heat will be absorbed, not released if reactions (1) and (2) both proceed in the forward direction.

In fact, the apparent extents of reactions (1) and (2) are 1.11 and –0.23 mol, respectively. It is not surprising that the apparent extent of reaction (2) is negative. The system initially contains only CH_4 and H_2O, and reaction (1) does not produce any CO_2. Since there isn't any CO_2 present initially, if reactions (1) and (2) were the only reactions taking place, reaction (2) could not take place as written, it could only proceed in the reverse direction.

The important point to remember is that all four reaction can occur, but without additional information, their true extents cannot be determined. The apparent extents of reactions (1) and (2) simply convey the net effect of all four reactions. Since reactions (1) and (2) were chosen as the complete set of mathematically independent reactions, the apparent extent of reaction (2) will have to be negative if any CO_2 is present in the system. In fact, using the apparent extents of reactions (1) and (2), the full composition is found to be 2.28% CH_4, 12.4% CO, 54.6% H_2, 26.4% H_2O, and 4.37% CO2.

The net heat released, calculated using equation (12), is –44 kcal, so as noted above, heat is indeed absorbed, and not released.