

Chapter 4 Answers

1. $\Delta_f S^\circ = -757.012 \text{ J mol}^{-1} \text{ K}^{-1}$ of $\text{CaAl}_2\text{Si}_2\text{O}_8$. This gives a $\Delta_f G^\circ = -4002.2 \text{ kJ mol}^{-1}$ when combined with $\Delta_f H^\circ$.
2. $\Delta_r H^\circ = -4.9 \text{ kJ mol}^{-1}$. Exothermic. $\Delta_r G^\circ = -5.1 \text{ kJ mol}^{-1}$. Albite should form spontaneously. Nepheline and quartz together at 25°C will not react; it is a truly metastable assemblage. They will react at high temperatures.
3. (a). $P = 1.01325 \text{ bar} = 0.101325 \text{ J cm}^{-3}$.
 $V = 0.0224141 \text{ m}^3 \text{ mol}^{-1} = 22414.1 \text{ cm}^3 \text{ mol}^{-1}$

$$R = \frac{0.101325 \times 22414.1}{273.15} \\ = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1}$$

- (b). energy is $\text{kg m}^3 \text{ s}^{-2}$; pressure is $\text{kg m}^{-1} \text{ s}^{-2}$
 so energy/pressure is m^3
 Therefore J bar^{-1} is a volume.

The SI convention is $1 \text{ J/Pa} = 1 \text{ m}^3$, so

$$1 \text{ J bar}^{-1} = 1 \times 10^{-5} \text{ m}^3 \\ = 10 \text{ cm}^3 \quad \text{so} \\ 1 \text{ cm}^3 = 0.10 \text{ J bar}^{-1}$$

4. $\Delta_r G^\circ = -2.613 \text{ kJ mol}^{-1}$. Nesquehonite more stable.
5. Diaspore>gibbsite>boehmite>corundum is the order of stability, with diaspore the most stable.
6. $\Delta_r G^\circ = -5.289 \text{ kJ mol}^{-1}$. Hematite more stable.
7. Using program STEAM, the coordinates of the four corners of the cycle are

T $^\circ\text{C}$	P bars	V $\text{cm}^3 \text{ mol}^{-1}$	S $\text{J mol}^{-1} \text{ K}^{-1}$
600	10,000	18.66	70.24
600	300	206.2	112.4
500	3602	22.32	70.24
500	175.8	311.5	112.4

The area under the 600°C isotherm, which is $T \Delta S$, is

$$q_{600} = T \Delta S \\ = 873.15(112.4 - 70.24) \\ = 36812 \text{ J mol}^{-1}$$

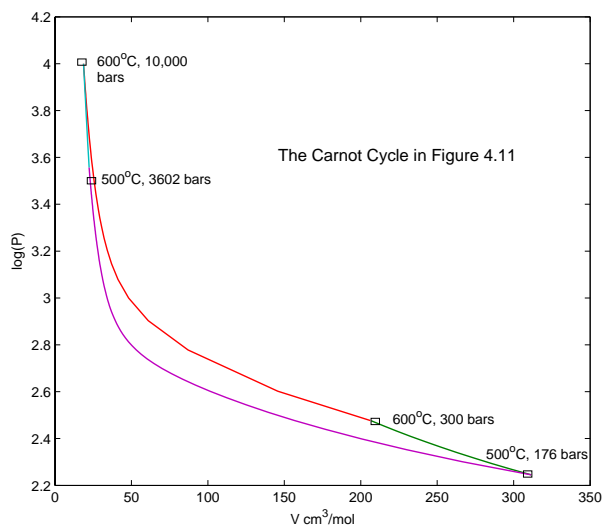


Figure 1: The Carnot cycle from Figure 4.11, replotted in $\log P$ - V space.

On the 500°C isotherm,

$$\begin{aligned} q_{500} &= T \Delta S \\ &= 773.15(70.24 - 112.4) \\ &= -32596 \text{ J mol}^{-1} \end{aligned}$$

so

$$\begin{aligned} q_{\text{net}} &= q_{600} + q_{500} \\ &= 36812 - 32596 \\ &= 4216 \text{ J mol}^{-1} \end{aligned}$$

Figure 4.11 was drawn with no thought as to what the P - V diagram would look like. In fact on the P - V plot the four curves are so close together as to be almost indistinguishable. To see the cycle better, $\log P$ is used in place of P in Figure 1.

8. This carnot cycle is shown in Figure 2. The four corners according to program STEAM are

T °C	P bars	V $\text{cm}^3 \text{ mol}^{-1}$	S $\text{J mol}^{-1} \text{ K}^{-1}$
600	100	691.39	124.39
600	55	1285.82	129.95
500	57.5	1067.6	124.39
500	31.4	1997.7	129.95

The area on the TS diagram is therefore

$$\begin{aligned} q &= 100(129.95 - 124.39) \\ &= 556 \text{ J mol}^{-1} \end{aligned}$$

The area on the PV diagram was found by determining a number of points along each curve, and finding the area under each with function `trapz` in MATLAB, which performs a trapezoidal integration. The area was found to be 560 J mol^{-1} , as shown in Figure 2. This obviously depends on how carefully you do it.

The fact that $q = -w$ does not mean that you have 100% heat to work conversion in a Carnot cycle. The heat lost from the cycle under the lower isotherm (500°C in this case) is “lost”, and is unavailable for doing work. Therefore the work accomplished by the Carnot heat engine (the area of the cycle) must always be less than the heat input (the area under the upper isotherm on a TS diagram), and the “efficiency”, or the fraction of heat transformed into work, is governed entirely by how far apart the upper and lower isotherms are. If q_2 is the area under the upper isotherm and q_1 is the area under the lower isotherm, the efficiency of this cycle is

$$\begin{aligned} \frac{w}{q_2} &= \frac{q_2 - q_1}{q_2} \\ &= \frac{T_2 - T_1}{T_2} \\ &= \frac{100}{873.15} \\ &= 0.115 \end{aligned}$$

or 11.5% . This doesn’t look very impressive, but the point is that this is an (unattainable) upper limit for the efficiency of any heat engine operating under these conditions. Also, in this case,

$$\frac{q_2}{q_1} = \frac{T_2}{T_1} = 1.2934$$

It is a short step from there to a definition of the absolute temperature scale, a step that is easy to follow now, but required a profound understanding (by Kelvin) to do it originally.

9.

$$z = 8.3 \left[\log \frac{x}{0.5} + \log \frac{(1-x)}{0.5} \right] + 12.5 \log \frac{y}{50}$$

where x varies from 0.01 to 0.99, and y varies from 25 to 350.

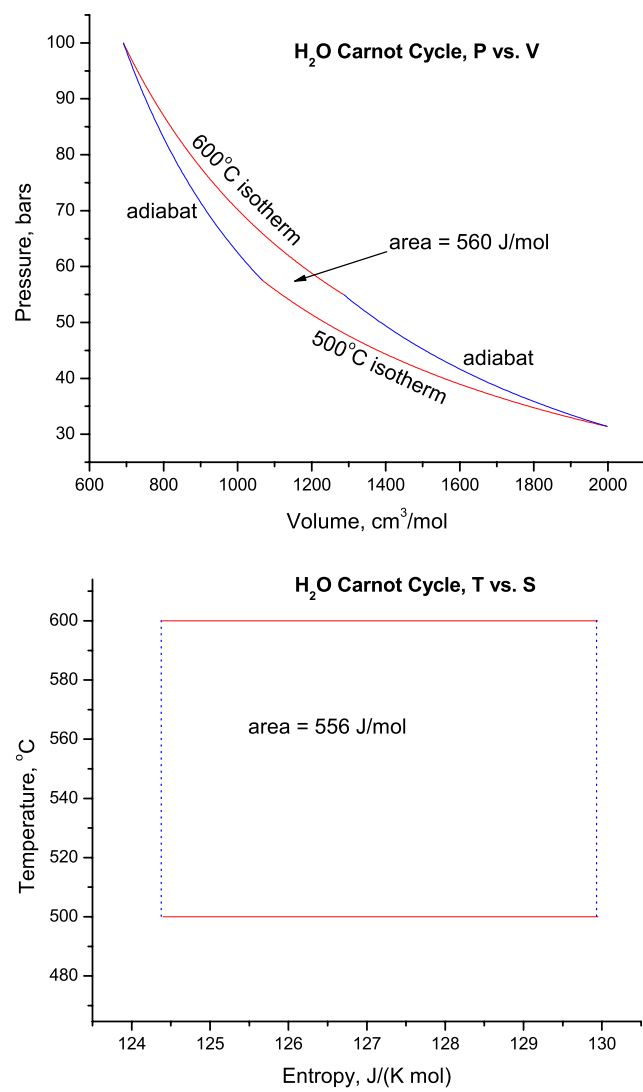


Figure 2: An H₂O Carnot cycle in PV and TS space