

12.8: The Thermodynamic Functions for Other Substances

Calculation of the change in the thermodynamic functions of any substance going reversibly from $P_1V_1T_1$ to $P_2V_2T_2$.

The first comforting thing to note is that *SUHAG* are all state functions, and therefore the change in their values is route-independent.

Entropy.

Entropy is a function of state (i.e. of PVT), but since PVT are related through the equation of state, it is necessary to specify only two of these quantities. Thus, for example if we express S as a function of T and P , infinitesimal increases in these will give rise to an infinitesimal increase in S given by

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad (12.8.1)$$

Now $\left(\frac{\partial S}{\partial T} \right)_P$ is (for a reversible process) $\frac{C_P}{T}$ (see equation 12.7.5), and $\left(\frac{\partial S}{\partial P} \right)_T$ is (by a Maxwell relation) equal to $-\left(\frac{\partial V}{\partial T} \right)_P$. If we know C_P as a function of temperature, and, if we know the equation of state, we can now calculate

$$S_2 - S_1 = \int_{T_1}^{T_2} C_P \frac{dT}{T} - \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T} \right)_P dP \quad (12.8.2)$$

This will enable us to calculate the change in entropy of a substance provided that we know how the heat capacity varies with temperature and provided that we know the equation of state.

For an ideal gas $\left(\frac{\partial V}{\partial T} \right)_P = R/P$, and so we obtain, for an ideal gas

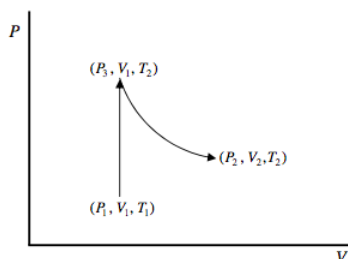
$$S_2 - S_1 = \int_{T_1}^{T_2} C_P \frac{dT}{T} - R \ln(P_2/P_1). \quad (12.8.3)$$

If we want to express the increase of entropy in terms of the change in temperature and volume, and of C_V , we can use $P_V = RT$ and $C_P = C_V + R$ to obtain

$$S_2 - S_1 = \int_{T_1}^{T_2} C_V \frac{dT}{T} + R \ln(V_2/V_1) \quad (12.8.4)$$

This agrees with what we had in the previous section for an isothermal expansion.

Here's another way of arriving at equation 12.9.4. We want to find the change in entropy of a mole of an ideal gas in going from (P_1, V_1, T_1) to (P_2, V_2, T_2) . Since the change in entropy is route-independent, we can choose any simple route for which the calculation is easy. Let's go at constant volume from (P_1, V_1, T_1) to (P_3, V_1, T_2) and then at constant temperature from (P_3, V_1, T_2) to (P_2, V_2, T_2) .



To go from (P_1, V_1, T_1) to (P_3, V_1, T_2) , the gas has to absorb an amount of heat $\int_{T_1}^{T_2} C_V dT$, and so its entropy increases by $\int_{T_1}^{T_2} C_V \frac{dT}{T}$. To go from (P_3, V_1, T_2) to (P_2, V_2, T_2) . The gas does work $RT_2 \ln(V_2/V_1)$ without any change in internal energy (because the internal energy of an ideal gas at constant temperature is independent of its volume), and therefore it absorbs this amount of heat. Therefore its entropy increases by $R \ln(V_2/V_1)$. Thus we arrive again at equation 12.9.4.

Example: If the substance is an ideal monatomic gas, then $C_P = \frac{5}{2}R$. From this we calculate

$$S_2 - S_1 = \frac{5}{2} R \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right) = R \ln \left[\left(\frac{T_2}{T_1} \right)^{5/2} \frac{P_1}{P_2} \right]. \quad (12.8.5)$$

Exercise: Go through the same analysis, but starting from $S = S(T, V)$. Show that the result you get for an ideal gas is the same as above. It will also, of course, necessarily be the same for any substance, though the equality of the expression you get with equation 12.9.2 may not be immediately apparent.

Exercise: The pressure and volume of an ideal monatomic gas are both doubled. What is the ratio of the new temperature to the old? What is the increase in the molar entropy?

(I make the answer $2.31 \times 10^4 \text{ J kmole}^{-1} \text{ K}^{-1}$.) Now try the same problem with an ideal diatomic gas. (I make the answer $3.46 \times 10^4 \text{ J kmole}^{-1} \text{ K}^{-1}$.)

Internal Energy and Enthalpy

These can be calculated if we know how C_V and C_P vary with temperature, because, by definition, $C_V = (\partial U / \partial T)_V$ and $C_P = (\partial H / \partial T)_P$.

Therefore

$$U_2 - U_1 = \int_{T_1}^{T_2} C_V dT \quad (12.8.6)$$

and

$$H_2 - H_1 = \int_{T_1}^{T_2} C_P dT. \quad (12.8.7)$$

Helmholtz and Gibbs Functions

Since $A = U - TS$, we have

$$A_2 - A_1 = U_2 - U_1 - T_2 (S_2 - S_1) - S_1 (T_2 - T_1). \quad (12.8.8)$$

In the special case of an ideal gas, we obtain

$$A_2 - A_1 = \int_{T_1}^{T_2} C_V dT - T_2 \int_{T_1}^{T_2} \frac{C_V dT}{T} - RT_2 \ln(V_2/V_1) - S_1 (T_2 - T_1). \quad (12.8.9)$$

Since $G = H - TS$, we have

$$G_2 - G_1 = H_2 - H_1 - T_2 (S_2 - S_1) - S_1 (T_2 - T_1) \quad (12.8.10)$$

In the special case of an ideal gas, we obtain

$$G_2 - G_1 = \int_{T_1}^{T_2} C_P dT - T_2 \int_{T_1}^{T_2} \frac{C_P dT}{T} - RT_2 \ln(P_1/P_2) - S_1 (T_2 - T_1). \quad (12.8.11)$$

There is, however, a serious difficulty with equations 12.9.9 and 12.9.11, in that, in order to calculate the change in the Helmholtz and Gibbs functions, we need to know the initial absolute entropy S_1 .

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