

## 11.6: The Standard State for Third-law Entropies

The standard state for entropies is essentially the same as the standard state for enthalpies. For liquids and solids, the standard state for entropies is identical to that for enthalpies: At any given temperature, the standard state is the most stable form of the substance at that temperature and a pressure of 1 bar.

For gases, the ideal gas standard state for entropy tabulations is the hypothetical ideal gas state at a pressure of 1 bar. A substance in a hypothetical ideal gas state is a creature of theory, and we obtain its thermodynamic properties from calculations that use the experimentally determined properties of the real gas. The idea behind these calculations is that we can—by calculation—remove the effects of intermolecular interactions from the measured properties. When we want the properties of the real gas, we put these effects back. From this perspective, we can say that a substance in its hypothetical ideal gas standard state has the entropy that the real gas would have if it behaved as an ideal gas at pressures of 1 bar and below.

In principle, this differs from the standard state chosen for enthalpy, because the enthalpy standard state is defined to be an arbitrary low pressure at which the substance behaves as an ideal gas. However, because the enthalpy of an ideal gas is independent of pressure, we can consider the standard state for either enthalpy or entropy to be the hypothetical ideal gas at a pressure of 1 bar. (Below, we write “ $HIG^o$ ” to designate this state.) Since the Gibbs free energy is defined by  $G = H - TS$ , we can also describe the standard state for the Gibbs free energy of gases as the hypothetical ideal gas at 1 bar.

To see precisely what we mean by the hypothetical ideal gas standard state, let us consider the conversion of one mole of a real gas, initially at pressure  $P$  and temperature  $T$ , to its hypothetical ideal gas state at 1 bar and the same temperature. We accomplish this in a three-step process. In the first step, we reversibly and isothermally expand the real gas to some arbitrary low pressure at which the real gas behaves ideally. The second step is purely conceptual: We suppose that the real gas changes into a hypothetical gas that behaves ideally. The third step is the reversible isothermal compression of the hypothetical ideal gas to a pressure of 1 bar. Letting  $A$  denote the gas, these steps are

1.  $A(\text{real gas}, P) \rightarrow A(\text{real gas}, P^* \approx 0)$
2.  $A(\text{real gas}, P^* \approx 0) \rightarrow A(\text{ideal gas}, P^* \approx 0)$
3.  $A(\text{ideal gas}, P^* \approx 0) \rightarrow A(HIG^o, P^o = 1 \text{ bar})$

We use the symbol “ $P^o$ ” to designate the standard-state pressure.  $P^o$  is a constant, whose value is 1 bar.

Let the enthalpy, entropy, and Gibbs free energy changes for the  $i^{\text{th}}$  step be  $\Delta_i \bar{H}$ ,  $\Delta_i \bar{S}$ , and  $\Delta_i \bar{G}$ . (We use the overbar to emphasize that the system consists of one mole of a pure substance. Since the superscript zero implies that  $H_A^o(HIG^o)$ , for example, is a property of one mole of  $A$  in its standard state, we omit the overbar from standard state properties.) From our expressions for  $dH$  and  $dS$  as functions of pressure and temperature, we have, at constant temperature,

$$(d\bar{H})_T = \left[ \bar{V} - T \left( \frac{\partial \bar{V}}{\partial T} \right)_P \right] dP$$

and

$$(d\bar{S})_T = - \left( \frac{\partial \bar{V}}{\partial T} \right)_P dP$$

For an ideal gas,

$$(d\bar{H})_T = 0$$

and

$$(d\bar{S})_T = -R/P$$

For step [GrindEQ\_1], the enthalpy change is

$$\Delta_1 \bar{H} = \int_P^{P^*} \left[ \bar{V} - T \left( \frac{\partial \bar{V}}{\partial T} \right)_P \right] dP$$

the entropy change is

$$\Delta_1 \bar{S} = \int_P^{P^*} - \left( \frac{\partial \bar{V}}{\partial T} \right)_P dP$$

We must evaluate the partial derivative using an equation of state that describes the real gas.

Step [\[GrindEQ\\_2\\_\]](#) is merely a change in our perspective; nothing actually happens to the gas. There is no enthalpy or entropy change:  $\Delta_2 \bar{S} = 0$  and  $\Delta_2 \bar{H} = 0$ .

For step [\[GrindEQ\\_3\\_\]](#), the enthalpy change is zero because the gas is ideal,  $\Delta_3 \bar{H} = 0$ . We evaluate the entropy change using the ideal gas equation; then

$$\Delta_3 \bar{S} = \int_{P^*}^{P^o} - \frac{R}{P} dP$$

Let  $\bar{H}_A(P)$ ,  $\bar{S}_A(P)$ , and  $\bar{G}_A(P)$  be the molar enthalpy, entropy, and Gibbs free energy of real gas  $A$  at pressure  $P$ . Let us express the enthalpy, entropy, and Gibbs free energy of the standard state substance relative to the corresponding properties of the constituent elements in their standard states at temperature  $T$ . Then the molar enthalpy, entropy, and Gibbs free energy of  $A$  in its hypothetical ideal gas standard state are  $\Delta_f H_A^o(HIG^o)$ ,  $\Delta_f S_A^o(HIG^o)$ , and  $\Delta_f G_A^o(HIG^o)$ . Since these are state functions, we have

$$\Delta_f H_A^o(HIG^o) = \bar{H}_A(P) + \Delta_1 \bar{H} + \Delta_2 \bar{H} + \Delta_3 \bar{H} = \bar{H}_A(P) + \int_P^{P^*} \left[ \bar{V} - T \left( \frac{\partial \bar{V}}{\partial T} \right)_P \right] dP$$

and

$$\Delta_f S_A^o(HIG^o) = \bar{S}_A(P) + \Delta_1 \bar{S} + \Delta_2 \bar{S} + \Delta_3 \bar{S} = \bar{S}_A(P) - \int_P^{P^*} \left( \frac{\partial \bar{V}}{\partial T} \right)_P dP - \int_{P^*}^{P^o} \frac{R}{P} dP$$

These equations relate the enthalpy and entropy of the hypothetical ideal gas standard state to the enthalpy and entropy of the real gas at pressure  $P$ , at the same temperature.

To evaluate the enthalpy change, we can use the virial equation for the volume of a real gas, set  $P^* = 0$ , and evaluate the resulting integral. (See problem 1a.) For the entropy, there is a complication. If we set  $P^* = 0$ , neither integral is finite. We can overcome this difficulty by choosing a small positive value for  $P^*$ . Then both integrals are finite, and the value of their sum remains finite in the limit as  $P^* \rightarrow 0$ . This occurs because the molar volume of any gas approaches the molar volume of an ideal gas at a sufficiently low pressure. (See problem 1.)

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