
Absolute Entropy

Third Law of thermodynamics

- **Absolute Entropies**

Absolute entropy of an ideal gas

Start with fundamental equation

$$dU = TdS - pdV$$

$$dS = \frac{dU + pdV}{T}$$

for ideal gas:

$$dU = C_V dT \quad \text{and} \quad p = \frac{nRT}{V}$$

$$dS = \frac{C_V dT}{T} + \frac{nR}{V} dV$$

At constant T, $dT=0$

$$dS_T = \frac{pdV}{T}$$

For an ideal gas, $pV = nRT$

$$dS_T = \frac{nRdV}{V}$$

At constant T

$$d(pV) = d(nRT) = 0$$

$$pdV = -Vdp$$

plugging into dS_T :

$$dS_T = -\frac{nRdp}{p}$$

This allows us to know how $S(p)$ if T held constant. Integrate!

Lecture 16

5.60/20.110/2.772

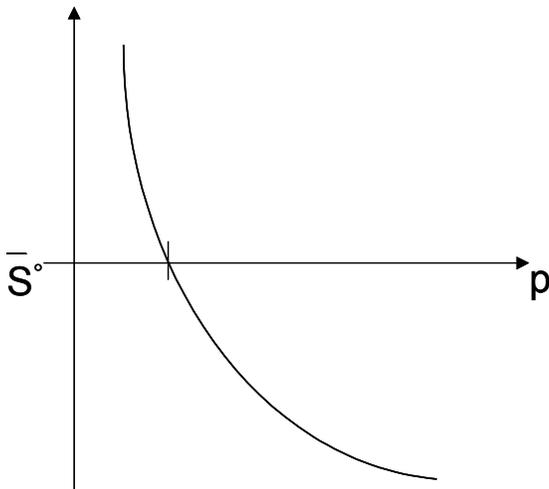
For an arbitrary pressure p ,

$$S(p, T) = S(p^\circ, T) - \int_{p^\circ}^p \frac{nR dp}{p} = S(p^\circ, T) - nR \ln \left(\frac{p}{p^\circ} \right)$$

where p° is some reference pressure which we set at 1 bar.

$$\Rightarrow S(p, T) = S^\circ(T) - nR \ln p \quad (p \text{ in bar})$$

$$\bar{S}(p, T) = \bar{S}^\circ(T) - R \ln p$$



But to finish, we still need $\bar{S}^\circ(T)$!

Suppose we had $\bar{S}^\circ(0\text{K})$ (standard molar entropy at 0 Kelvin)

$$dH = TdS + Vdp$$

$$dH = C_p dT$$

for ideal gas

$$C_p dT = TdS + Vdp$$

$$dS = \frac{C_p}{T} dT - \frac{V}{T} dp$$

Then using $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$

we should be able to get $\bar{S}^o(T)$. Integrating over dS eqn, assuming C_p constant over T range:

$$dS = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{p_1}^{p_2} \frac{nR}{p} dp$$

So then

$$\begin{aligned} \Delta S &= C_p \ln\left(\frac{T_2}{T_1}\right) - nR \ln\left(\frac{p_2}{p_1}\right) \\ &= C_p \ln\left(\frac{T_2}{T_1}\right) - nR \ln p \end{aligned} \quad \text{for } p = 1\text{bar}$$

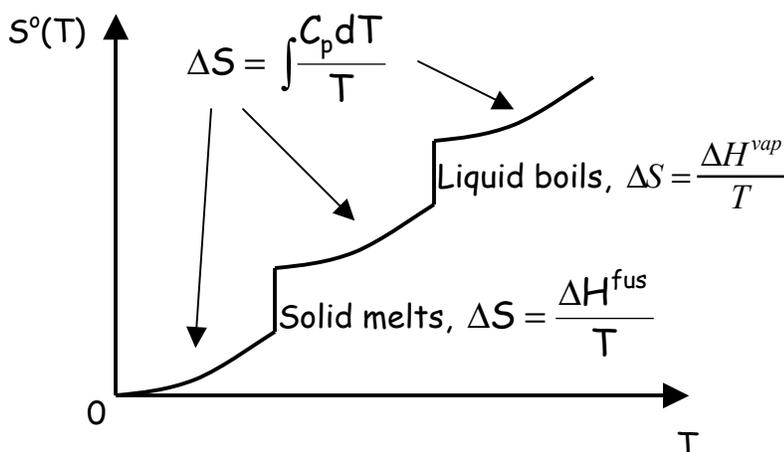
Given $C_p, T_1, p_1, \rightarrow T_2, p_2$, can calculate ΔS .

We will use $T=0K$ as a reference point.

Consider the following sequence of processes for the substance A:

$$A(s, 0K, 1bar) = A(s, T_m, 1bar) = A(l, T_m, 1bar) = A(l, T_b, 1bar) = A(g, T_b, 1bar) = A(g, T, 1bar)$$

$$\bar{S}(T, 1bar) = \bar{S}^o(0K) + \int_0^{T_m} \frac{\bar{C}_p(s)dT}{T} + \frac{\Delta\bar{H}_{fus}}{T_m} + \int_{T_m}^{T_b} \frac{\bar{C}_p(l)dT}{T} + \frac{\Delta\bar{H}_{vap}}{T_b} + \int_{T_b}^T \frac{\bar{C}_p(g)dT}{T}$$



Since ΔS^0 is *positive* for each of these processes, the entropy must have its smallest possible value at 0 K. If we take $\bar{S}^0(0\text{K}) = \text{zero}$ for every pure substance in its crystalline solid state, then we could calculate the entropy at any other temperature.

This leads us to the Third Law of Thermodynamics:

• THIRD LAW:

First expressed as **Nernst's Heat Theorem**:

Nernst (1905):

As $T \rightarrow 0\text{ K}$, $\Delta S \rightarrow 0$ for all isothermal processes in condensed phases

More general and useful formulation by **M. Planck**:

Planck (1911):

As $T \rightarrow 0\text{ K}$, $S \rightarrow 0$ for every chemically homogeneous substance in a perfect crystalline state

Justification:

- ① It works!
- ② Statistical mechanics (5.62) allows us to calculate the entropy and indeed predicts $\bar{S}^0(0\text{K}) = 0$.

This leads to the following interesting corollary:

It is impossible to decrease the temperature of any system to $T = 0\text{ K}$ in a finite number of steps.

How can we rationalize this statement?

Recall the fundamental equation, $dU = T dS - p dV$

$$dU = C_v dT$$

$$\text{For 1 mole of ideal gas, } P = RT/V$$

so

$$C_v dT = T dS - (RT/V) dV$$

$$dS = C_v d(\ln T) + R d(\ln V)$$

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For a spontaneous adiabatic process which takes the system from T_1 to a lower temperature T_2 ,

$$\Delta S = C_v \ln (T_2/T_1) + R \ln (V_2/V_1) \geq 0$$

but if $T_2 = 0$, $C_v \ln (T_2/T_1)$ equals minus infinity !

Therefore $R \ln (V_2/V_1)$ must be greater than plus infinity, which is impossible. Therefore no actual process can get you to $T_2 = 0$ K.

But you can get *very very* close!

In W. Ketterle's experiments on "Bose Einstein Condensates" (recent MIT Nobel Prize in Physics), atoms are cooled to nanoKelvin temperatures ($T = 10^{-9}$ K) ... but not to 0 K !

Some *apparent* violations of the third law (but which are not !)

Any disorder at $T = 0$ K gives rise to $S > 0$

- mixed crystals

If have an unmixed crystal, N atoms in N sites:

$$\Omega = \frac{N!}{N!} = 1$$

$$S = k \ln 1 = 0$$

But if mixed crystal:

N_A of A

N_B of B

$N_A + N_B = N$

$$\Omega = \frac{N!}{N_A! N_B!}$$

$$S = k \ln \frac{N!}{N_A! N_B!}$$

Use Stirling's approx:

$$\ln N! = N \ln N - N$$

$$S = k(N \ln N - N - N_A \ln N_A + N_A - N_B \ln N_B + N_B)$$

$$= -k(-N \ln N + N_A \ln N_A + N_A + N_B \ln N_B)$$

Using mole fractions: $N_A = x_A N$, $N_B = x_B N$

$$\Delta S_{mix} = -nR [X_A \ln X_A + X_B \ln X_B] > 0 \text{ Always !!! Even at } T=0K$$

But a mixed crystal is not a pure substance, so the third law is not violated.

- Any impurity or defect in a crystal also causes $S > 0$ at $0 K$
- Any orientational or conformational degeneracies such as in a molecular crystal causes $S > 0$ at $0 K$, for example in a carbon monoxide crystal, two orientations are possible:

