Fundamental Equations, Absolute Entropy, and The Third Law

- Fundamental Equations relate functions of state to each other using 1st and 2nd Laws

  1st law with expansion work: $dU = đq - p_{ext}dV$

  need to express đq in terms of state variables because đq is path dependent

  Use 2nd law: $đq^{rev} = TdS$

  For a reversible process $p_{ext} = p$ and $đq = đq^{rev} = TdS$

  So…… ** $\boxed{dU = TdS - pdV}$ **

  This fundamental equation only contains state variables

  Even though this equation was demonstrated for a reversible process, the equation is always correct and valid for a closed (no mass transfer) system, even in the presence of an irreversible process. This is because U, T, S, p, and V are all functions of state and independent of path.

  AND The "best" or "natural" variables for U are S and V,

  ** $\boxed{U(S,V)}$ **

$$** \boxed{U(S,V)} **$$

From $dU = TdS - pdV \Rightarrow$ $$** \boxed{\left(\frac{\partial U}{\partial S}\right)_V = T \quad ; \quad \left(\frac{\partial U}{\partial V}\right)_S = -p} **$$

We can write similar equations for <u>enthalpy</u>

$H = U + pV \Rightarrow dH = dU + d(pV) = dU + pdV + Vdp$

inserting $dU = TdS - pdV$

$$\Rightarrow ** \boxed{dH = TdS + Vdp} **$$

The natural variables for H are then <u>S and p</u>

$$** \boxed{H(S,p)} **$$

From $dH = TdS + Vdp \Rightarrow$ $$** \boxed{\left(\frac{\partial H}{\partial S}\right)_p = T \quad ; \quad \left(\frac{\partial H}{\partial p}\right)_S = V} **$$

We can use these equations to find how S depends on T.

From $dU = TdS - pdV \Rightarrow$ $$\boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V}{T}}$$

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- Absolute Entropies

Absolute entropy of an ideal gas

From $dU = TdS - pdV \Rightarrow dS = \frac{dU + pdV}{T}$

At constant T, $dU=0 \Rightarrow dS_T = \frac{pdV}{T}$

For an ideal gas, $pV = nRT \Rightarrow dS_T = \frac{nRdV}{V}$

At constant T $d(pV) = d(nRT) = 0 \Rightarrow pdV = -Vdp$

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

For an arbitrary pressure p,

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

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

$\Rightarrow$ $S(p,T) = S^o(T) - nR \ln p$ (p in bar)

$$\boxed{\overline{S}(p,T) = \overline{S}^o(T) - R\ln p \quad (p \text{ in bar})}$$

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

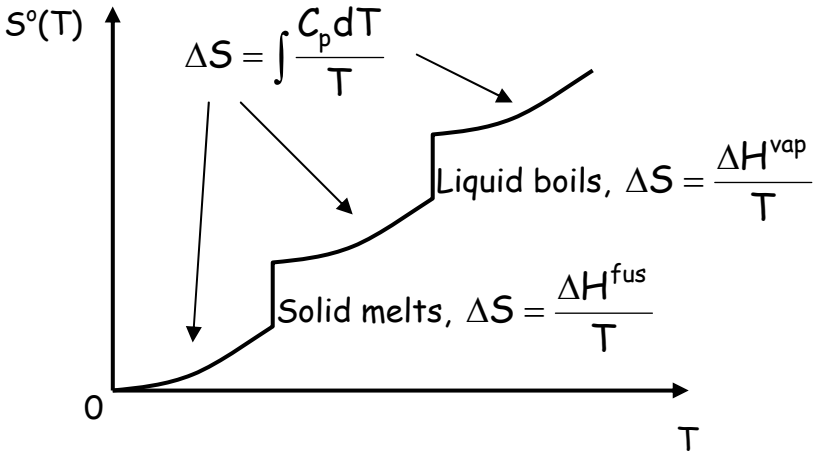
Suppose we had $\overline{S}^o(0K)$ (standard molar entropy at 0 Kelvin)

Then using $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$ we should be able to get $\overline{S}^o(T)$

Consider the following sequence of processes for the substance A:

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

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



Since ΔS^0 is *positive* for each of these processes, the entropy must have its smallest possible value at 0 K. If we take $\overline{S}^{\circ}(0K)$ = 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!!!

THIRD LAW:

First expressed as Nernst's Heat Theorem:

- Nernst (1905): As $T \rightarrow 0$ K , $\Delta S \rightarrow 0$ for all isothermal processes in condensed phases

More general and useful formulation by M. Planck:

- Planck (1911): As $T \rightarrow 0$ 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 $\overline{S}^{\circ}(0K) = 0$.

This leads to the following interesting corollary:

It is <u>impossible</u> to decrease the temperature of <u>any</u> system to T = 0 K in a finite number of steps

How can we rationalize this statement?

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

$dU = C_v\,dT$ For 1 mole of ideal gas, $P = RT/V$

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

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

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

Another consequence of the Third Law is that

It is impossible to have T=0K.

How can we rationalize the alternate statement?

Consider the calculation of S starting at T=0K

$$S(s,T,1bar) = \int_0^T \frac{C_p(s)dT}{T}$$

to prevent a singularity at T=0, $C_p \to 0$ as $T \to 0$ K

in fact, experimentally $C_p = \gamma T + AT^3 + ...$

That is, the heat capacity of a pure substance goes to zero as T goes to zero Kelvin and this is experimentally observed.

Combining the above with $dT = đq_p/C_p$, at T=0 any infinitesimally small amount of heat would result in a finite temperature rise.

In other words, because $C_p \to 0$ as $T \to 0$ K, the heat $đq_p$ needed to achieve a temperature rise dT, ($đq_p=C_pdT$) also goes to zero at 0 K. If you somehow manage to make it to 0 K, you will not be able to maintain that temperature because any stray heat from a warmer object nearby will raise the temperature above zero, unless you have perfect thermal insulation, which is impossible.

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

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

  - For example in mixed crystals

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

But a mixed crystal is <u>not</u> 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 is in a molecular crystal causes S > 0 at 0 K, for example in a carbon monoxide crystal, two orientations are possible:

C O C O C O C O C O C O C O
C O C O C O C O C O O C C O
C O C O C O O C C O C O C O
C O C O C O C O C O C O C O