# Chapter Six: Fundamental Equations, Absolute Entropy, and The Third Law

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

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

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

   Use 2$^{nd}$ law: $đq^{rev} = TdS$

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

   So……    $dU = \cancel{TdS} - pdV$

   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,

**\*\*\*\***
**\*\*\*\***     $U(S,V)$

$U(S,V)$

From $dU = TdS - pdV \Rightarrow$ **\*\***

$$\left(\frac{\partial U}{\partial S}\right)_V = T \; ; \quad \left(\frac{\partial U}{\partial V}\right)_S = -p \quad \text{**}$$

We can write similar equations for <u>enthalpy</u> $H = U$

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

inserting $dU = TdS - pdV$

$\Rightarrow$ **\*\*\*\***  $dH = TdS + Vdp$

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

**\*\*\*\***   $H(S,p)$

From $dH = TdS + Vdp \Rightarrow$ **\*\***

$$\left(\frac{\partial H}{\partial S}\right)_p = T \; ; \quad \left(\frac{\partial H}{\partial p}\right)_S = V \quad \text{**}$$

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

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

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 $\Rightarrow$ $\boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V}{T}}$

From dH = TdS + Vdp $\Rightarrow$ $\boxed{\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p = \frac{C_p}{T}}$

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- <u>Absolute Entropies</u>

Absolute entropy of an <u>ideal gas</u>

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

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

For an <u>ideal</u> gas, $pV = nRT \Rightarrow dS_T = \dfrac{nRdV}{V}$

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

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

For an arbitrary pressure p,

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

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

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

$$\boxed{\overline{S}(p,T) = \overline{S}^o(T) - R\ln p \quad \text{(p in bar)}}$$
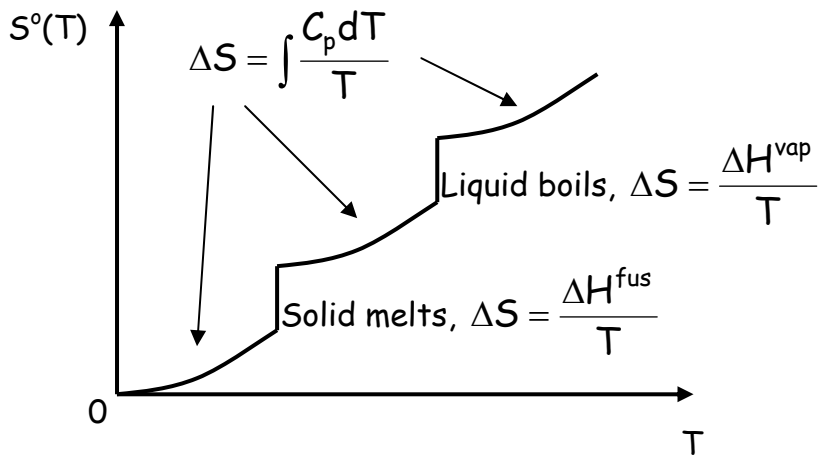
But to finish, we still need $\overline{S}^o(T)$ !

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

Then using $\left(\dfrac{\partial S}{\partial T}\right)_{p} = \dfrac{C_p}{T}$ we should be able to get $\overline{S}°(T)$

Consider the following sequence of processes for the substance A:

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

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



$S°(T)$

$\Delta S = \int \dfrac{C_p dT}{T}$

Liquid boils, $\Delta S = \dfrac{\Delta H^{vap}}{T}$

Solid melts, $\Delta S = \dfrac{\Delta H^{fus}}{T}$

$0$

$T$

Since $\Delta S°$ is positive for each of these processes, the entropy must have its smallest possible value at 0 K. If we take $S°(0K) =$ 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
<u>Third Law</u>
     !!!

## THIRD LAW:
First expressed as Nernst's Heat Theorem:
•
for all isothermal

     Nernst (1905): As $T \rightarrow 0$ K , $\Delta S \rightarrow 0$ 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:
♍ It works!
♎ Statistical mechanics (5.62) allows us to calculate the
entropy and indeed predicts $S°(0K) = 0$.
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

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

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

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

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 $C_p \rightarrow 0$ as $T \rightarrow 0$ K, the heat $đq_p$ needed to achieve a temperature rise dT, ($đq_p = C_p dT$) 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 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