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5.60 Thermodynamics & Kinetics
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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: $dU = \delta q - p_{\text{ext}}dV$

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

Use 2nd law: $\delta q^{\text{rev}} = TdS$

For a reversible process $p_{\text{ext}} = p$ and $\delta q = \delta q^{\text{rev}} = TdS$

So..... **** $dU = TdS - pdV$ ****

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 ,

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

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

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

We can write similar equations for enthalpy

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



inserting $dU = TdS - pdV$

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

The natural variables for H are then S and p

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

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

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

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

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

- Absolute Entropies

Absolute entropy of an ideal gas

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

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

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

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

So

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

For an arbitrary pressure p ,

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

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

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

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

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

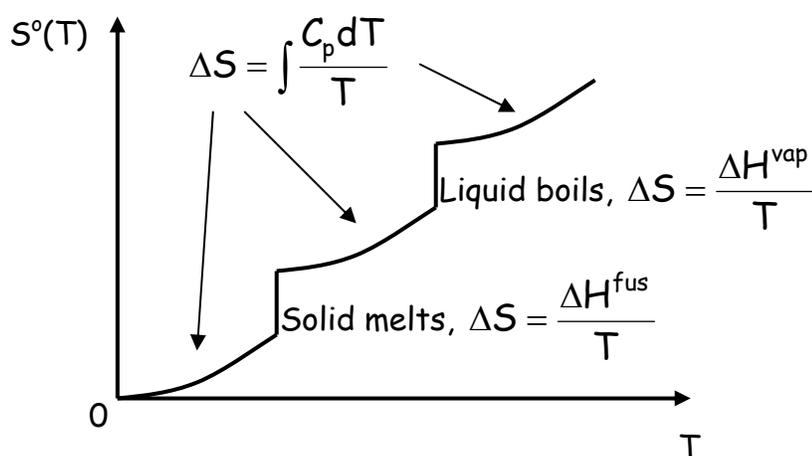
Suppose we had $\bar{S}^\circ(0\text{K})$ (standard molar entropy at 0 Kelvin)

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

Consider the following sequence of processes for the substance A:

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

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



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

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, $dU = T dS - p dV$

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

$$\text{so } C_v dT = T dS - (RT/V) dV$$

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

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 $T_2 = 0 \text{ K}$.

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 $T=0$ K.

How can we rationalize the alternate statement?

Consider the calculation of S starting at $T=0$ K

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

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

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

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 $dT = \delta q_p / C_p$, 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 δq_p needed to achieve a temperature rise dT , ($\delta q_p = C_p dT$) 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

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

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:

