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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

\[ dU = dq - p_{ext}dV \]

1st law with expansion work: \( dU = dq - p_{ext}dV \)

need to express \( dq \) in terms of state variables because \( dq \) is path dependent

Use 2nd law: \( dq^{rev} = TdS \)

For a reversible process \( p_{ext} = p \) and \( dq = dq^{rev} = TdS \)

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 \( V \).

\[ **U(S,V)** \]
**U(S,V)**

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

We can write similar equations for **enthalpy**

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

inserting \(dU = TdS - pdV\)

\(\Rightarrow\) **\(dH = TdS + Vdp\)**

The natural variables for \(H\) are then **\(S\) and \(p\)**

**H(S,p)**

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

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

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

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

Absolute entropy of an ideal gas

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

\[
\frac{dS_T}{p} = -\frac{nRdp}{p}
\]

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 \( p^\circ \) is some reference pressure which we set at 1 bar.

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

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

But to finish, we still need \( S^\circ(T) \)!

Suppose we had \( S^\circ(0K) \) (standard molar entropy at 0 Kelvin)

Then using \( \frac{\partial S}{\partial T} \bigg|_p = \frac{C_p}{T} \) we should be able to get \( S^\circ(T) \)
Consider the following sequence of processes for the substance A:

\[ A(s, 0K, 1\text{bar}) = A(s, T_m, 1\text{bar}) = A(\ell, T_m, 1\text{bar}) = A(\ell, T_b, 1\text{bar}) = A(g, T_b, 1\text{bar}) = A(g, T, 1\text{bar}) \]

\[ \overline{S}(T, 1\text{bar}) = \overline{S}^0(0K) + \int_0^{T_m} C_p(s) \frac{dT}{T} + \frac{\Delta H_{\text{fus}}}{T_m} + \int_{T_m}^{T_b} C_p(\ell) \frac{dT}{T} + \frac{\Delta H_{\text{vap}}}{T_b} + \int_{T_b}^{T} C_p(g) \frac{dT}{T} \]

Since \( \Delta S^0 \) is positive for each of these processes, the entropy must have its smallest possible value at 0 K. If we take \( \overline{S}^0(0K) = 0 \) 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 \( T \to 0 \) K, \( \Delta S \to 0 \) for all isothermal processes in condensed phases
More general and useful formulation by M. Planck:

- Planck (1911): As $T \to 0 \text{ K}$, $S \to 0$ 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 $\overline{S}(0\text{K}) = 0$.

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  \quad 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 \((T = 10^{-9} \text{ K})\) ... but not to 0 K!

Another consequence of the Third Law is that

\[
\text{It is impossible to have } T=0K.
\]

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 \(T=0\), \(C_p \to 0\) 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 \(dT = dq_p/C_p\) , 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 \(dq_p\) needed to achieve a temperature rise \(dT\), \((dq_p=C_p\,dT)\) 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 \( T = 0 \text{ K} \) gives rise to \( S > 0 \)

• For example in mixed crystals

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

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 \( 0 \text{ K} \)

• Any orientational or conformational degeneracies such is in a molecular crystal causes \( S > 0 \) at \( 0 \text{ K} \), for example in a carbon monoxide crystal, two orientations are possible:

\[
\begin{align*}
\text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{O} & \quad \text{C} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{O} & \quad \text{C} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} \\
\end{align*}
\]