- Connecting 1st and 2nd "Laws" of Thermodynamics

- 3rd "Law" of Thermodynamics

  ↳ assigns an <u>absolute value</u> to entropy, S, under specific conditions

S, U, H

  → consistency between "continuum" and "microscopic" views

  → Entropy is the only thermo. function with an <u>absolute value</u>

  → All other thermo functions are relative to some <u>reference value</u> or <u>reference state</u>.

1st & 2nd "Laws"

closed sys. (no mass exchange)

$$dU = đq + đw$$

$$dU = đq - p_{ext}\, dV$$

Reversible Process:

$$dU = đq_{rev} - p\, dV$$

$$dS = \frac{đq_{rev}}{T}$$

$$\boxed{dU = T\,dS - p\,dV}$$

closed system

$$\boxed{dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV}$$

constant volume: $dV = 0$

$$dS = \frac{1}{T}\,dU$$

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

I. G. $pV = nRT$

$$dS^{ig} = \frac{1}{T} dU + \frac{p}{T} dV$$

$$dU^{ig} = C_v \, dT$$

$$dS^{ig} = \frac{1}{T} C_v \, dT + nR \frac{dV}{V}$$

$$dS^{ig} = C_v \frac{dT}{T} + nR \, d(\ln V)$$

$$\boxed{dS^{ig} = C_v \, d(\ln T) + nR \, d(\ln V)}$$

$T_1 \rightarrow T_2$

$V_1 \rightarrow V_2$

$$\Delta S^{ig} = \underbrace{C_v \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)}_{-\infty} > 0$$

Spontaneously Irreversibly $\Delta S^{ig} > 0$

$$nR \ln\left(\frac{V_2}{V_1}\right) > +\infty$$

T_1 close to 0 K

T_2 is 0 K

$$\Delta S^{ig} = C_v \ln\left(\frac{T_2}{T_1}\right)$$

$\ln(0) = -\infty$

$e^{-\infty} \to 0$

$\frac{1}{\infty} \to 0$

We can never get to 0 K!

$$dS = \frac{dq_{rev}}{T} = \frac{C_p(T)\,dT}{T}$$

Approach 0 K.

$C_p(T) \to 0$ as $T \to 0$ K

small T

$dq = C_p(T)\,dT$

$$dT = \frac{dq}{C_p(T)}$$

← Let's go to "small" T (0 K)

Can't get to 0K!!!

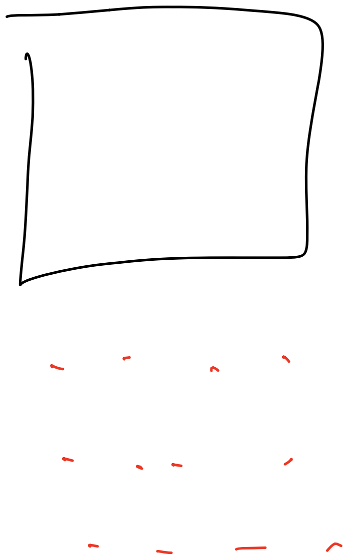
10^{-9} Kelvin Wolfgang Ketterle (MIT) Nobel Prize

Bose-Einstein Condensate

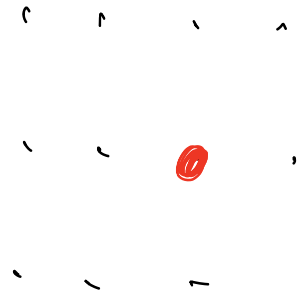
Third "Law"

→ $S = 0$ J/K at 0 Kelvin for a perfect crystal

$dS = \frac{dq_{rev}}{T}$; $S = k_B \ln W$; $S = -k_B \sum p_i \ln p_i$



$W = 1$



$W = 12$

Criteria for Spontaneity

Irreversibility

Isolated System (no q; no w)

$$dS > 0$$

$(\Delta S > 0)$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV$$

$dU = 0$

$dV = 0$

at equilibrium $(dS)_{U,V} = 0$

$(dS)_{U,V} \geq 0$ criterion (Inequality)

natural variables of S

Isolated system

$dU = TdS - pdV$

natural variables of U ?

$U(S,V) \Leftarrow$