

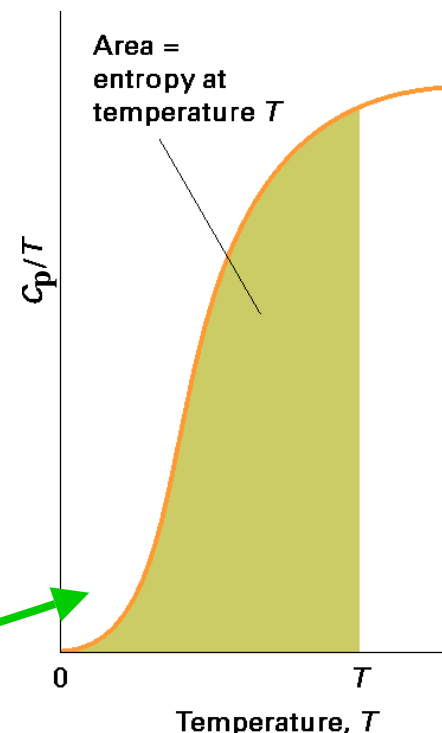
The third law: Absolute entropies

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

Because there is an absolute zero for temperature, the entropy for any state can be calculated ...
if we know $S(0K)$.

$T_1 = 0K$

$$S(T) = \int_0^T \frac{C_p(T)}{T} dT + S(0K)$$



We also defined entropy statistically:

$W(T)$ = number of accessible microstates at T

$$S(T) = k \ln W(T)$$

$W(T)$ depends on T through the Boltzmann distribution (fewer states accessible at low T):

$$P_n \propto e^{-\Delta E/kT}$$



This definition gives us a useful $S(T = 0K)$

Flip three coins			$P =$ probability	$W = \#$ of microstates	$S = k \ln W$
“isoenergetic”	H H H	A	1/8	1	0 k
	H H T	B	3/8	3	1.10 k
	H T H				
	T H H				
	T T H	C	3/8	3	1.10 k
	T H T				
	H T T				
	T T T	D	1/8	1	0 k

If there is only one accessible microstate, the entropy of the system (macrostate) is given by:

$$S = k \ln W = k \ln 1 = 0$$

This is consistent with our view of entropy as a measure of disorder. No disorder (only one possible state) $\Rightarrow S = 0$ @ $T = 0$ K

The third law of thermodynamics

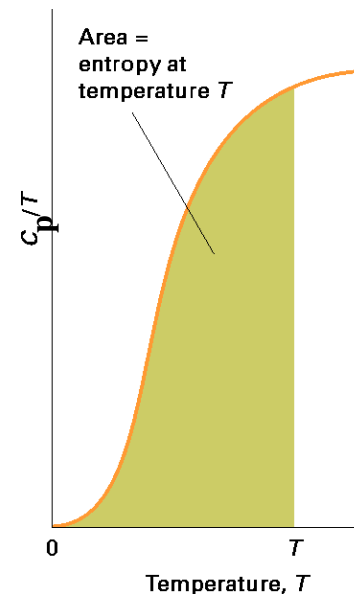
$S = 0$ for all perfectly crystalline materials at $T = 0$ K

If there is only one possible arrangement of atoms
(i.e., in a perfect crystal):

$$S = k \ln W = k \ln 1 = 0$$

Since every substance has a finite (nonzero) heat capacity

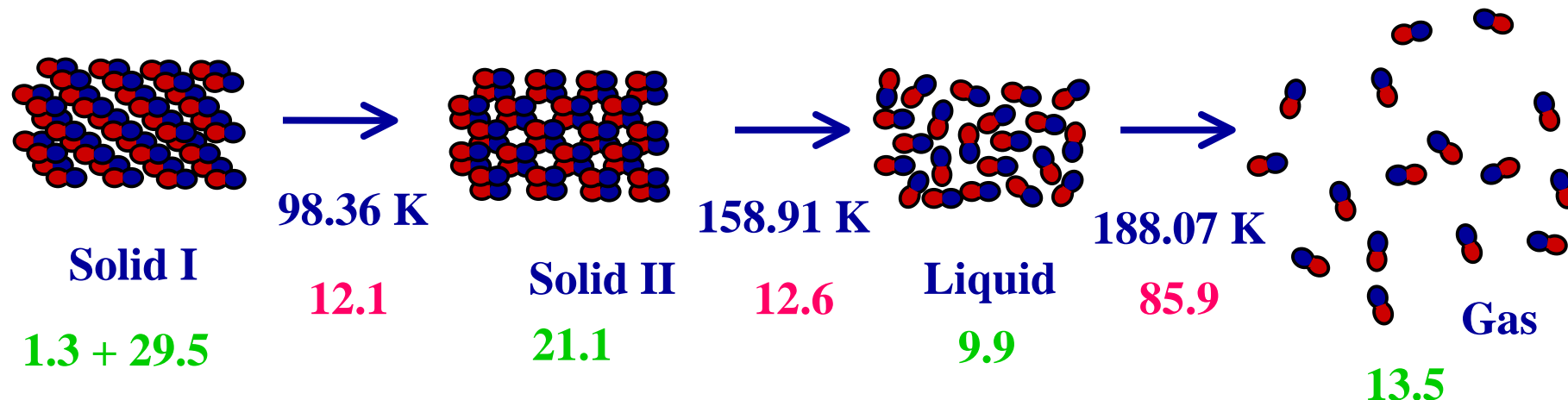
$$\text{and } S(T) = \int_0^T \frac{C_p(T)}{T} dT + \overset{=0}{S(0K)}$$



\Rightarrow except for a perfect crystal at absolute zero,
every substance has a finite **positive entropy**

**Standard absolute or “third law” molar entropies are
tabulated, generally at 1 bar and 298 K (\ominus)**

One can calculate the molar entropy of HCl



$$\text{Sum: } S_{298.15}^{\ominus} = 185.9 \text{ J K}^{-1} \text{mol}^{-1}$$

Solid I $\left\{ \begin{array}{l} S = \int C_p \, d\ln T \text{ from } 0 \text{ K to } 16 \text{ K using Debye } T^3\text{-law: } C_p = aT^3 \\ S = \int C_p \, d\ln T \text{ from } 16 \text{ K to } 98.36 \text{ K using experimental } C_p \end{array} \right.$

$S = \Delta H/T$ for each phase transition

Solid II $S = \int C_p \, d\ln T \text{ from } 98.36 \text{ K to } 158.91 \text{ K using experimental } C_p$

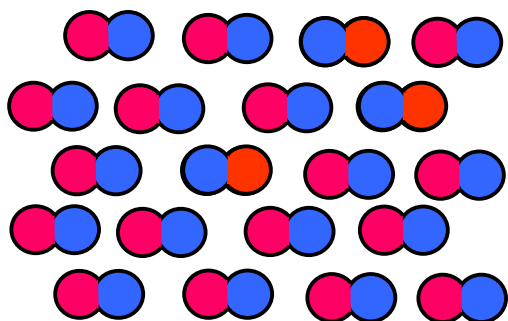
Liquid $S = \int C_p \, d\ln T \text{ from } 158.91 \text{ K to } 188.07 \text{ K using experimental } C_p$

Gas $S = \int C_p \, d\ln T \text{ from } 188.07 \text{ K to } 298.15 \text{ K using experimental } C_p$

The exception:

An imperfect crystal still has residual entropy

a) Consider CO



If there were no preferred orientation $W = 2^N$

For one mole: $W = 2^{N_A}$

$$S = k \ln W$$

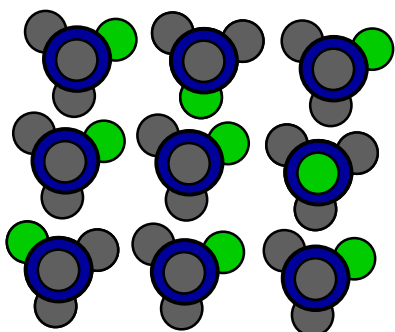
$$= k \ln 2^{N_A}$$

$$= N_A k \ln 2$$

$$= R \ln 2 = 5.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Actual value:
 $4.2 \text{ J K}^{-1} \text{ mol}^{-1}$

b) Consider CH_3D



No dipole moment, same number of electrons

No preferred orientation!

$W = 4^N$ or for one mole $W = 4^{N_A}$

$$S = R \ln 4 = 11.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

Actual value:
 $11.7 \text{ J K}^{-1} \text{ mol}^{-1}$



The three laws of thermodynamics

Atkins

Moore

1.

$\Delta U = q + w$
Energy Conservation

The internal energy of
an isolated system is
constant

You can't construct
a *perpetuum mobile*
that generates
energy from nothing

2.

$\Delta S \geq 0$
everything tends
toward increasing
disorder

The entropy of the
universe tends to
increase

You can't construct a
machine that does
nothing but convert
heat into work

3.

$S > 0$ except for
perfect crystals at
 $T = 0 \text{ K}$

The entropy of a
perfectly crystalline
substance is zero at
 $T = 0 \text{ K}$

You can never
reach absolute
zero

Summary:

The energy of the universe is constant; the entropy
of the universe tends always toward a maximum.

Rudolf Julius Clausius (1822-1888)

