

# 14. Crystals

Einstein's model

Debye model

entropy and disorder in crystals

# CRYSTALS -

Monatomic crystal containing  $N$  atoms can be regarded as a giant molecule, with  $3N - 6 \approx 3N$  degrees of vibrational freedom.

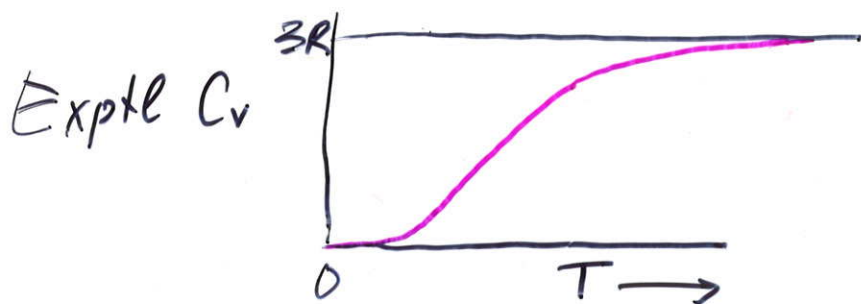
Classical harmonic vibration

$$\bar{E} = kT \quad \text{K.E.} = \frac{1}{2}kT \quad \text{P.E.} = \frac{1}{2}kT$$

Total vibrational energy of a crystal =  $3NkT$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3Nk \quad (\text{Dulong + Petit})$$

At low  $T$  observe not a constant  $C_V$  but one which approaches zero:



Canonical partition function for a system of independent distinguishable elements:

$$E = \epsilon_{v_1} + \epsilon_{v_2} + \epsilon_{v_3} + \dots + \epsilon_{v_{3N}}$$

$$g_i = \sum_{v_i=1}^{\infty} e^{-\beta \epsilon_{v_i}}$$

$$Q = \sum_j e^{-E_j/kT} = g_1 \cdot g_2 \cdot g_3 \cdot \dots \cdot g_{3N}$$

$$A = -kT \ln Q = -kT (\ln g_1 + \ln g_2 + \dots + \ln g_{3N})$$

$$E = kT^2 \left[ \frac{\partial \ln Q}{\partial T} \right]_V = kT^2 \left( \frac{\partial \ln g_1}{\partial T} \right) + \dots$$

$$E = \bar{E}_1 + \bar{E}_2 + \dots + \bar{E}_{3N}$$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \underbrace{C_{V1}}_{\left( \frac{\partial \bar{E}_1}{\partial T} \right)_V} + C_{V2} + \dots$$

$$S = \frac{E - A}{T} = \left( \frac{\bar{E}_1}{T} + k \ln g_1 \right) + ( \quad ) + \dots$$

Einstein's model:

Einstein's theory of low temperature heat capacity of solids

One harmonic oscillator in 1-D

$$u = h\nu/kT$$

$$g(u) = \frac{1}{1 - e^{-u}}$$

$$\bar{E}(u) = \frac{h\nu e^{-u}}{1 - e^{-u}} = \frac{h\nu}{e^u - 1}$$

$$C_V(u) = \left( \frac{\partial \bar{E}}{\partial T} \right)_V = \frac{k u^2 e^u}{(e^u - 1)^2}$$

$$S = \frac{\bar{E}}{T} + k \ln g = \frac{k u}{e^u - 1} - k \ln(1 - e^{-u})$$

Einstein: let each atom be harmonically bound to its equilibrium position in the lattice. Neglect effect of other (neighboring) atoms on the motion of a given atom.

In the limit that frequencies  $\nu_1, \nu_2, \dots, \nu_{3N}$  are equal:

Because motion in 3 dimensions are independent and atoms are non-interacting, we can consider a crystal as

$3N$  one-D harmonic oscillators with the same  $\nu$

Since they are distinguishable particles,

$$Q = q^{3N} \\ = \left( \frac{1}{1 - e^{-u}} \right)^{3N}$$

$$A = -kT \ln Q = -kT (\ln q_1 + \ln q_2 + \dots)$$

$$E = kT^2 \left[ \frac{\partial \ln Q}{\partial T} \right]_V = kT^2 \left( \frac{\partial \ln q_1}{\partial T} \right) + \dots$$

$$E = \bar{E}_1 + \bar{E}_2 + \dots + \bar{E}_{3N} = 3N\bar{E}$$

For one HO

$$c_v(u) = \left( \frac{d\bar{E}}{dT} \right)_V = k u^2 \frac{e^{-u}}{(e^u - 1)^2}$$

$$u = \frac{h\nu}{kT} \\ = \frac{\theta}{T}$$

At high  $T$ ,  $u \rightarrow 0$

$$\lim_{u \rightarrow 0} C_v = 3Nk \lim_{u \rightarrow 0} \frac{u^2 e^{-u}}{(e^u - 1)^2}$$

$$= 3Nk \lim_{u \rightarrow 0} \left[ 1 - \frac{1}{12} u^2 + \dots \right]$$

$$= 3Nk \left[ 1 - \frac{1}{12} \left( \frac{\theta}{T} \right)^2 \right]$$

$\rightarrow 3Nk$  as  $T \rightarrow \infty$  Dulong-Petit behavior at high  $T$

At low  $T$ ,  $u \rightarrow \infty$   $e^u - 1 \approx e^u$

$$\lim_{u \rightarrow \infty} C_V = 3Nk \lim_{u \rightarrow \infty} u^2 e^{-u} \Rightarrow 0 \text{ as } T \rightarrow 0$$

for low  $T$ ,  $C_V = 3Nk \left(\frac{\theta}{T}\right)^2 e^{-\theta/T}$ ,  $\theta \equiv \frac{h\nu}{k}$

This is qualitatively the correct behavior as observed in crystals.

Improve Einstein's model:

If the crystal is viewed as a giant molecule it would have  $3N - 6 \approx 3N$  vibrational modes of vibration with different frequencies.

$$\begin{aligned} -\frac{A}{kT} = \ln Q &= \ln q(u_1) + \ln q(u_2) + \dots \\ &= \ln \frac{1}{1 - e^{-u_1}} + \dots \\ &= -[\ln(1 - e^{-u_1}) + \dots] \end{aligned}$$

Since the vibrational frequencies are closely spaced (a large number of them!) let us introduce a continuous function, the spectral density function

$g(\nu) d\nu =$  no. of normal vibrational frequencies in the range  $\nu$  and  $\nu + d\nu$

$$3N = \int_0^{\infty} g(\nu) d\nu$$

Now replace the sum over  $3N$  terms by an integral

$$\ln Q = - \int_0^{\infty} \ln(1 - e^{-u}) g(\nu) d\nu$$

$$E = \bar{E}_1 + \bar{E}_2 + \dots$$

$$= \frac{h\nu_1}{e^{u_1} - 1} + \dots$$

$$= kT \frac{u_1}{e^{u_1} - 1} + \dots \quad \leftarrow \text{replace sum by integral}$$

$$E = kT \int_0^{\infty} \frac{u g(\nu) d\nu}{e^u - 1}$$

heat capacity

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = k \int_0^{\infty} \frac{u^2 e^u g(\nu) d\nu}{(e^u - 1)^2}$$

$$S = \frac{E - A}{T}$$

### Debye's Model:

Obtain  $g(\nu)$  function without discrete atomic nature of the crystal. Treat all the frequencies from the viewpoint of elastic or acoustic waves.

Consider a crystal in the shape of a cube of edge  $L$ . Let the sides be clamped so that the boundary conditions for the vibrations is that the displacements are zero at the walls.

Each standing wave is of the form

$$\sin \frac{\pi s_x x}{L} \cdot \sin \frac{\pi s_y y}{L} \cdot \sin \frac{\pi s_z z}{L}$$

where  $s_x, s_y, s_z$  are positive integers.

$$\text{Let } s^2 = s_x^2 + s_y^2 + s_z^2$$

The wavelength is  $\lambda = \frac{2L}{s}$

$$\left[ \begin{aligned} s &= \frac{2L\nu}{c} \\ ds &= \frac{2L}{c} d\nu \end{aligned} \right]$$

The frequency is  $\nu = \frac{c}{\lambda} = c \left( \frac{s}{2L} \right)$

The number of allowed sets of integers  $(s_x, s_y, s_z)$  between  $s$  and  $s+ds = \frac{\pi s^2}{2} ds$

$\therefore$  The number of allowed frequencies for standing waves between  $\nu$  and  $\nu+d\nu$  is

$$\frac{\pi}{2} \left( \frac{2L\nu}{c} \right)^2 \frac{2L}{c} d\nu = \frac{4\pi V}{c^3} \nu^2 d\nu$$

where  $V = L^3$  of course.

There are two kinds of waves in rigid materials:

Transverse waves with velocity  $c_t$   
 2 directions of polarization for any given direction of propagation (i.e., 2 possible waves for any given  $(s_x, s_y, s_z)$ )

Longitudinal waves with velocity  $c_l$

$$\therefore g(\nu) d\nu = \left( \frac{2}{c_t^3} + \frac{1}{c_l^3} \right) 4\pi V \nu^2 d\nu$$

Define average velocity  $c$

$$\frac{3}{c^3} = \frac{2}{c_t^3} + \frac{1}{c_l^3}$$



$$g(\nu)d\nu = \frac{12\pi V}{c^3} \nu^2 d\nu$$

Assume that there is an upper limit for the allowed vibrations which is determined by the requirement that the total number of vibrations is  $3N$

$$\int_0^{\nu_D} g(\nu)d\nu = 3N = \int_0^{\nu_D} \frac{12\pi V}{c^3} \nu^2 d\nu$$

$$\therefore \nu_D^3 = \frac{3}{4\pi} \frac{N}{V} c^3 \quad \text{or}$$

$$g(\nu)d\nu = \frac{9N}{\nu_D^3} \nu^2 d\nu \quad \text{for } 0 \leq \nu \leq \nu_D$$

$$g(\nu) = 0 \quad \text{for } \nu > \nu_D$$

Corresponding to the Debye frequency  $\nu_D$  is a characteristic temperature, the Debye temperature

$$\Theta_D = \frac{h\nu_D}{k}$$

$$u = h\nu/kT$$

$$\nu^2 d\nu = \left(\frac{kT}{h}\right)^3 u^2 du$$

at which  $\frac{h\nu}{kT}$  becomes  $\frac{\Theta_D}{T} = u_D$

$$g(\nu)d\nu = 9N \left(\frac{T}{\Theta_D}\right)^3 u^2 du = \frac{9N}{u_D^3} u^2 du$$

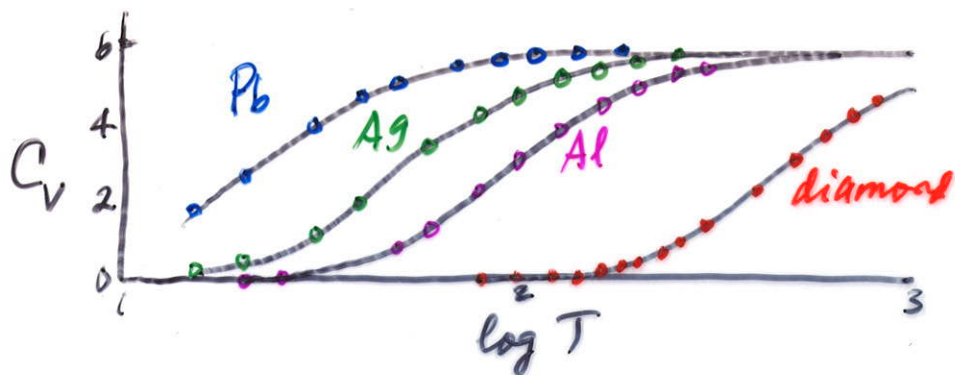
Put this spectral density function into

$$C_V = k \int \frac{u^2 e^{-u}}{(e^u - 1)^2} g(\nu)d\nu$$

to get

$$\frac{C_V}{3Nk} = \frac{3}{u_D^3} \int_0^{u_D} \frac{u^4 e^{-u}}{(e^u - 1)^2} du = \text{Debye function}$$

a universal functional form for atomic solids



The entire shape of the  $C_v$  curve is reproduced if a single parameter, the Debye temperature is fixed:

Pb	90.3 K
Ag	213
Al	389
C	1890

Of course, the Debye function has the correct behavior as  $T \rightarrow \infty$  ( $C_v \rightarrow 3R$ )

And as  $T \rightarrow 0$  the Debye function approaches

$$\frac{C_v}{3Nk} = 3 \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\infty} \frac{u^4 e^{-u}}{(e^u - 1)^2} du \Rightarrow \frac{4\pi^5}{15} \left( \frac{T}{\Theta_D} \right)^3 = 27.93 \left( \frac{T}{\Theta_D} \right)^3$$

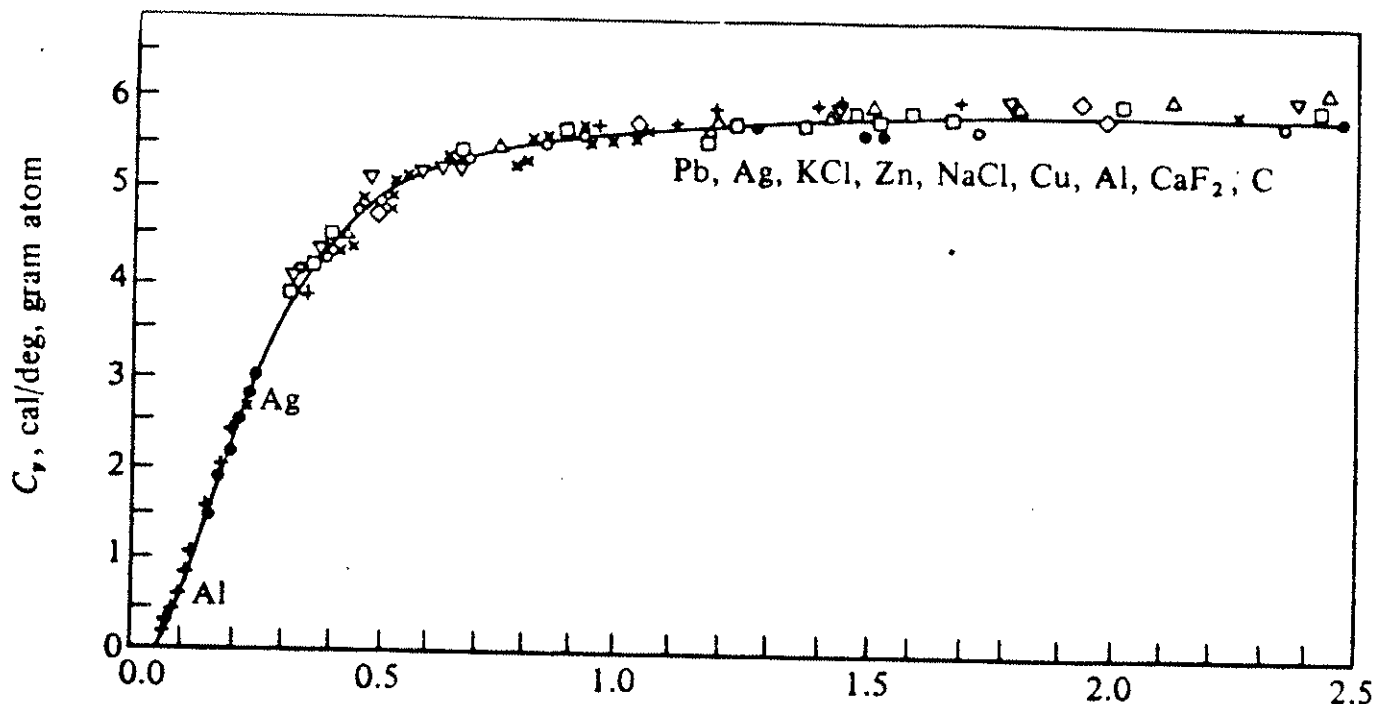
This is known as the "T cubed" law, one of the important results of Debye theory.  $C_v = 0$  at 0 K.

The foregoing did not include electronic heat capacity.

The  $T^3$  law is important. For a pure phase, the entropy change with temperature is

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

$C_p$  has to be properly behaved in the  $T \rightarrow 0$  region otherwise  $\Delta S$  blows up.  $C_p = AT^3$  from Debye theory



**FIGURE 23.1** Gram-Atomic Heat Capacities of Several Crystalline Solids. The solid curve represents the heat capacity of a perfect monatomic crystal as a function of  $T/\Theta_D$  according to the Debye model. Data for several solids are plotted, the temperatures being appropriately scaled for optimal fit. [Adapted from Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, 1960), p. 145.]

**TABLE 23.1.** Periodic Table showing Debye Characteristic Temperatures  $\Theta_D$  ( $^{\circ}\text{K}$ ) for some Crystalline Elements

Li	Be											B	C	N	O	F
430	1160												1860			
Na	Mg											Al	Si	P	S	Cl
160	330											398	580		180	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
99	230		430		405	350	453	445	413	315	235	125	362			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Sb	I
	170		280		375		400	370	275	215	165	100	165	204		106
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
		150	213	245	315	300	250	285	233	185	90	96	86	111		

# What about molecular solids?

Benzene 12 atoms  $\rightarrow$  30 internal vibrations which are well-known from spectroscopy

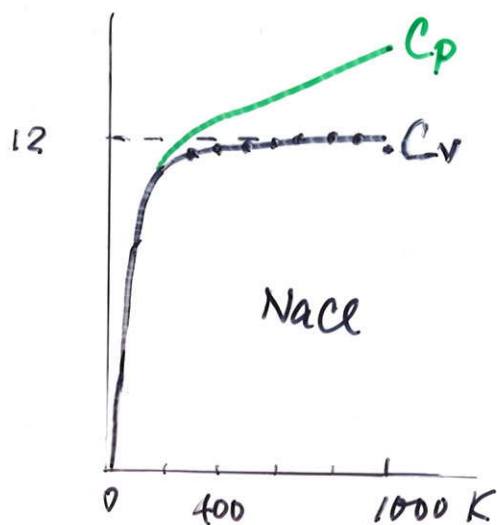
treated as acoustical modes by Debye theory

$\leftarrow$  6 degrees of freedom (translation + rotation) of each molecule

Add to  $(C_v)_{\text{Debye}} = 3 Nk \left[ \frac{4\pi^5}{15} \left( \frac{T}{\theta_D} \right)^3 \right]$  the internal contributions from vibrations

$$C_v = (C_v)_{\text{Debye}} + R \sum_{i=1}^{30} C_v(u_i)$$

$C_p$  can go beyond  $3Nk$  per atom when the lattice vibrations are relatively large (at high temperatures) because of the anharmonicity of lattice vibrations. However no such data for  $C_v$ .



3 R per atom  
6 R per NaCl

# ENTROPY and DISORDER in CRYSTALS

$$S = k \ln t$$

$t =$  no. of configurations

If there are  $N$  molecules at definite lattice sites and each molecule can have  $n$  physically distinguishable orientations with respect to the crystallographic axes

then the number of PHYSICALLY DISTINGUISHABLE CONFIGURATIONS of the system is

$$n^N$$

This is based on the different lattice sites are distinguishable, the state with molecule at site  $i$  "up" and the molecule at site  $j$  "down" is physically distinguishable from  $i$ ="up"  $j$ ="up"  $i$ ="down"  $j$ ="up" and  $i$ ="down"  $j$ ="down".

In a perfect crystal where all molecules are perfectly aligned - there is only one configuration,

$$t = 1 \quad S = k \ln 1 = 0$$

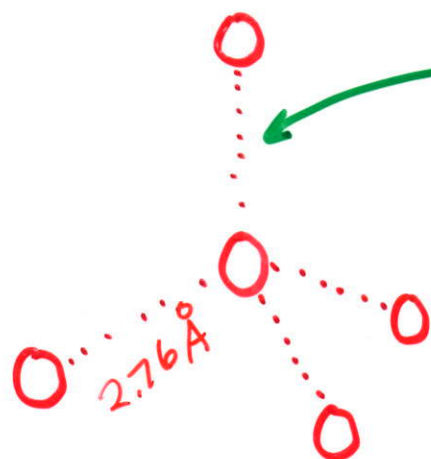
On the other hand if all orientations of molecules are found, then  $t = n^N$

$$S = k \ln n^N = Nk \ln n$$

CO

For CO there could be some residual entropy due to some disorder in the crystal which may remain at 0 K.

If  $n=2$   $S = k \ln 2^N = Nk \ln 2 = 1.38 \frac{\text{cal}}{\text{mole deg}}$   
completely ordered  $S=0$ , random order  $S = 1.38$



H atom is in one or the other well

∴ 2 possible positions for each H atom

N H<sub>2</sub>O molecules

2N H atoms

Number of configurations =  $2^{2N}$

if no restrictions about how many H atoms around a given O atom can be in the closer or farther well.

If a given O atom can only have 2 H atoms in the closer well (looks like an isolated H<sub>2</sub>O molecule) and the other 2 H atoms in the farther well,

$$\frac{4!}{(4-2)! 2!} = 6 \text{ possible ways of choosing } 2 \text{ out of } 4$$

But  $2^4 = 16$  possible configurations of 4 H atoms around a given O atom altogether

∴ Fraction of acceptable arrangements is  $(6/16)$  for any given O atom

$S = 1.1$  is obtained experimentally for CO  
 $\therefore$  there is a slight amount of ordering in the crystal.

How does the disorder get frozen in?

Although theoretically the perfect crystal (single configuration) can be achieved, as the crystal is cooled to very low temperatures there is not enough energy at these low temperatures for the CO molecules to rotate into the proper most stable configuration.

NNO

Similarly NNO has a residual entropy of about  $Nk \ln 2$  and  $\text{FCIO}_3$   $Nk \ln 4$



almost ( $2.42$  instead of  $2.75 \text{ cal deg}^{-1} \text{ mole}^{-1}$ )  
F can point along 4 different directions

$\text{H}_2\text{O}$

Ice on the other hand is found to have a residual entropy  $\approx Nk \ln 3/2$  ( $0.82$  instead of  $0.806$ ). Ice has a hexagonal structure with each O surrounded tetrahedrally by 4 other O at a distance  $2.76 \text{ \AA}$ .

Because of H-bonding there are 2 near  $\text{H}_2$  and 2 distant  $\text{H}_2$  around each O atom

There are  $2^4 = 16$  possible configurations for the 4 H atoms. Of these  $4!/(4-2)!2! = 6$  satisfy the H-bonding conditions, that is 6 ways for the molecule to be oriented so that the short O-H bonds are pointed along 2 of the 4 O-O directions. Thus, the total number of configurations is  $t = 2^{2N} \left(\frac{6}{16}\right)^N = \left(\frac{3}{2}\right)^N$  for N oxygens and 2N hydrogens

$$t = 2^{2N} \left(\frac{6}{16}\right)^N = \left(\frac{3}{2}\right)^N$$

**ANOTHER WAY OF LOOKING AT IT :**

Consider individual  $\text{H}_2\text{O}$  molecules

# Possible orientations of a given  $\text{H}_2\text{O}$  molecule :  
 4 O-H directions around O  
 Choose 2 of them  
 $= \frac{4!}{(4-2)!2!} = 6$

Along a given O...O direction, the probability that the other  $\text{H}_2\text{O}$  will be using this direction to point its own O-H bond is  $\frac{2}{4}$  H directions  $= \frac{1}{2}$

$\therefore$  The probability for a given  $\text{H}_2\text{O}$  orientation is  $\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)$   
 $\uparrow$  first  $\uparrow$  second  
 H H

Total number of possible configurations of  $N$   $\text{H}_2\text{O}$  molecules is

$$t = 6^N \left(\frac{1}{4}\right)^N = \left(\frac{3}{2}\right)^N$$

$$S = k \ln t = k \ln \left(\frac{3}{2}\right)^N = Nk \ln \frac{3}{2} = .806 \text{ cal deg}^{-1} \text{ mol}^{-1}$$



How is "residual entropy" measured?

A. From spectroscopic data and the eqns

$$S = \frac{E - A}{T} \text{ where } E = \underbrace{E_{tr}}_{\frac{3}{2}NkT} + NkT^2 \frac{d \ln q_{int}}{dT}$$

$$A = -NkT \left( \ln \frac{q_{tr}}{N} + 1 \right) - NkT \ln q_{int}$$

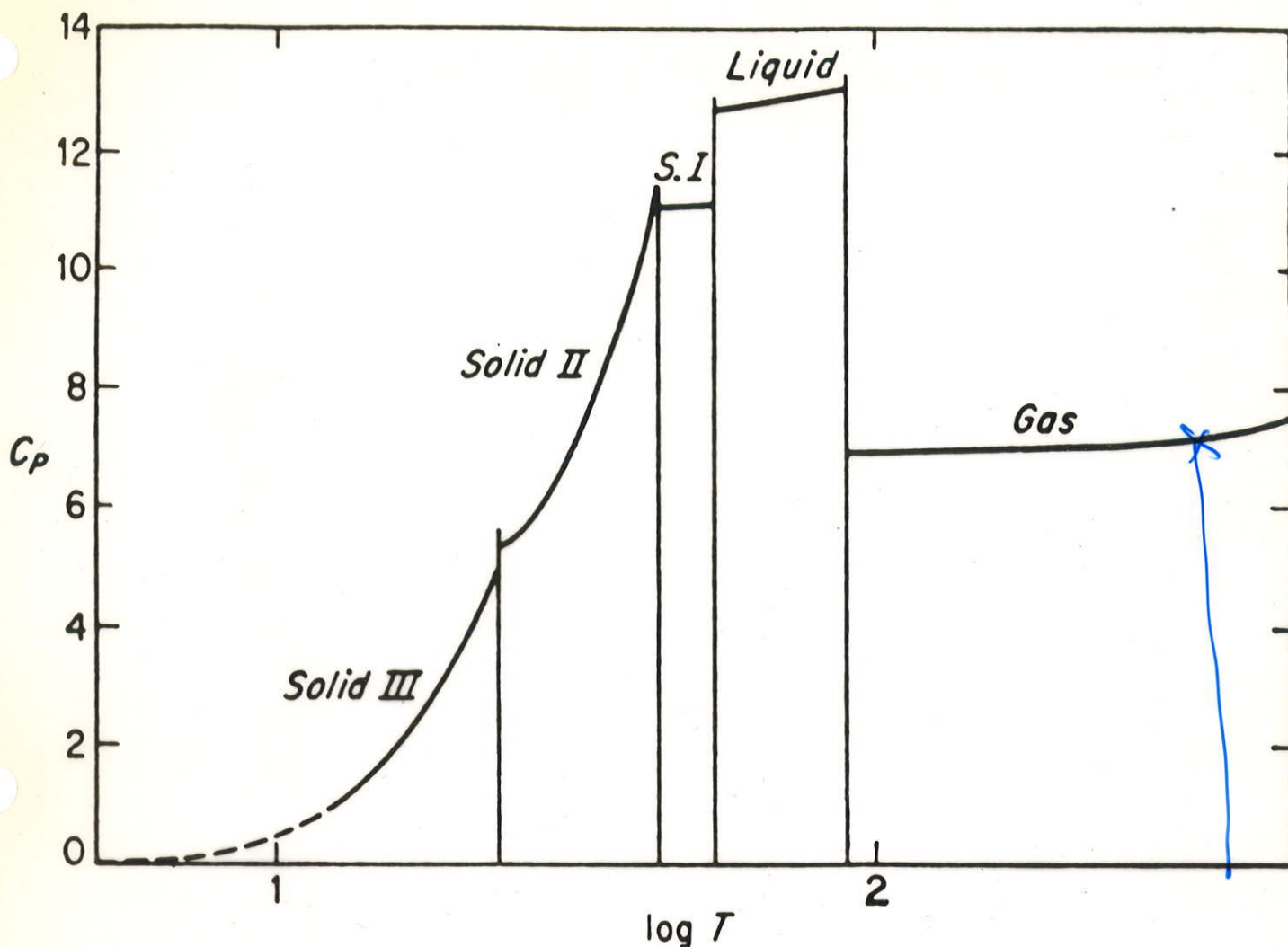
for a gas at 298.16 K and 1 atm can be calculated. For CO this is  $47.301 \text{ cal deg}^{-1} \text{ mol}^{-1}$  (the absolute entropy of the gas according to statistical mechanics)

B. The entropy of the gas can also be determined "calorimetrically", i.e., by starting with the solid at 0 K and measuring the heat capacity as a function of temperature, and finding the entropies for the various phase transitions by  $\frac{\Delta H}{T}$  from the measured

$\Delta H_{\text{phase transition}}$	Example CO	$\Delta S$
0 $\rightarrow$ 11.70 K	Debye extrapolation $\Theta_D = 79.5 \text{ K}$	0.458
11.70 $\rightarrow$ 61.55	graphical integration	9.632
Transition	151.3 / 61.55 solid I $\rightarrow$ solid II	2.457
61.55 $\rightarrow$ 68.09	graphical integration	1.228
Fusion	149.7 / 68.09 solid II $\rightarrow$ liquid	2.933
68.09 $\rightarrow$ 81.61	graphical integration	2.611
Vaporization	1443.6 / 81.61 liquid $\rightarrow$ gas	17.689
	correction for non-ideal gas at 81.61	37.01 $\pm$ 0.1
81.61 $\rightarrow$ 298.16		0.21
		9.0

"Calorimetric" entropy =  $46.2 \text{ cal deg}^{-1} \text{ mol}^{-1}$

$47.301 - 46.2$  of CO gas at 298.16 K = residual entropy =  $1.10 \text{ cal deg}^{-1} \text{ mol}^{-1}$



The molal heat capacity of oxygen.

### THE ENTROPY OF OXYGEN

0–14°K, extrapolation.....	0.54
14–23.66°K, solid III, graphical.....	1.500
Transition, $^{22.42}_{23.66}$ .....	0.948
23.66–43.76°K, solid II, graphical.....	4.661
Transition, $^{177.6}_{43.76}$ .....	4.058
43.76–54.39°K, solid I, graphical.....	2.397
Fusion, $^{106.3}_{54.39}$ .....	1.954
54.39–90.13°K, liquid, graphical.....	6.462
Vaporization $^{1628.8}_{90.13}$ .....	18.07
<b>Total, <math>s_{90.13}</math> (gas, 1 atm), cal/deg.....</b>	<b>40.59</b>

# Comparison of "calorimetric" and spectroscopic entropies at 298 K?

	A Calculated from spectroscopic data	B calorimetric based on third law		
N <sub>2</sub>	45.79	45.79	}	
O <sub>2</sub>	49.03	49.05		
HCl	44.64	44.66		very close or the same
HBr	47.48	47.48		
HI	49.4	49.4		
CO	47.32	45.93	}	
NO	43.75	43.06		very small dipole moment
H <sub>2</sub> O	45.10	44.29	← 0.81 hydrogen-bonding	
D <sub>2</sub> O	46.66	45.85	← 0.81 hydrogen-bonding	
H <sub>2</sub> S	46.44	46.44	}	
NH <sub>3</sub>	44.10	44.10		very close or same
CH <sub>4</sub>	36.61	36.62	}	
CH <sub>3</sub> D	39.49	36.73		← 2.76 Nk ln 4
CO <sub>2</sub>	47.55	47.55	}	
N <sub>2</sub> O	48.50	47.12		← 1.38 Nk ln 2
C <sub>2</sub> H <sub>4</sub>	47.35	47.35	}	
CH <sub>3</sub> Br	57.99	57.99		same

When dipole moment is small, as T is lowered less and less energy is available for the molecules to rotate and orient themselves, hence CO NO N<sub>2</sub>O become frozen at their random up or down arrangements. Similarly for CH<sub>3</sub>D where there are 4 possible directions for the C-D