Thermodynamics of Materials
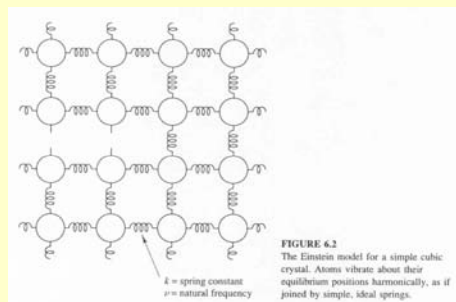
11th Lecture

2008. 4. 7 (Mon.)

Einstein's Model of a Crystal (only vibrational K.E.)

harmonic oscillator

FIGURE 6.2
The Einstein model for a simple cubic crystal. Atoms vibrate about their equilibrium positions harmonically, as if joined by simple, ideal springs.

k = spring constant
ν = natural frequency

$$\varepsilon_i = \left(i + \frac{1}{2} \right) \hbar \nu$$

Evaluate partition function.

$$P = \sum_{i=0}^{r} e^{-(\varepsilon_i / kT)} = \sum_{i=0}^{r} e^{-\left[\left(i + \frac{1}{2} \right) \hbar \nu / kT \right]}$$

$$P = \sum_{i=0}^{r} e^{-i(\hbar \nu / kT)} \cdot e^{-(1/2)(\hbar \nu / kT)} = e^{-(1/2)(\hbar \nu / kT)} \sum_{i=0}^{r} e^{-i(\hbar \nu / kT)}$$

Einstein's Model of a Crystal

$$P = e^{-(1/2)(\hbar\nu/kT)} \sum_{i=0}^{r} e^{-i(\hbar\nu/kT)}$$

$$\text{Let } x = \exp\left(-\frac{\hbar\nu}{kT}\right) \quad \rightarrow \quad \sum_{i=0}^{\infty} x^i = \frac{1}{1-x}$$

$$\sum_{i=0}^{\infty} \left(e^{-(\hbar\nu/kT)}\right)^i = \frac{1}{1 - e^{-(\hbar\nu/kT)}}$$

$$P = ? \qquad\qquad P = \frac{e^{-(1/2)(\hbar\nu/kT)}}{1 - e^{-(\hbar\nu/kT)}}$$

$$\ln P = ? \qquad \ln P = -\frac{1}{2}\frac{\hbar\nu}{kT} - \ln\left[1 - e^{-(\hbar\nu/kT)}\right]$$

Einstein's Model of a Crystal

$$\ln P = -\frac{1}{2}\frac{\hbar\nu}{kT} - \ln\left[1 - e^{-(\hbar\nu/kT)}\right]$$

Derive Helmholz Free Energy.

$$F = -N_0 kT \ln P$$

$3N_0$ bonds (particles) in a simple cubic crystal

$$F = -3N_0 kT \ln P = \frac{3}{2} N_0 \hbar\nu + 3N_0 KT \ln\left(1 - e^{-(\hbar\nu/kT)}\right)$$

Einstein's Model of a Crystal

$$\ln P = -\frac{1}{2}\frac{\hbar\nu}{kT} - \ln\left[1 - e^{-(\hbar\nu/kT)}\right]$$

Derive Entropy.
$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = 3\frac{N_0\hbar\nu}{T}\left[\frac{e^{-(\hbar\nu/kT)}}{1 - e^{-(\hbar\nu/kT)}}\right] - 3N_0 k \ln\left(1 - e^{-(\hbar\nu/kT)}\right)$$

Derive Internal Energy.
$$U = F + TS$$

$$U = F + TS = \frac{3}{2}N_0\hbar\nu\left[\frac{1 + e^{-(\hbar\nu/kT)}}{1 - e^{-(\hbar\nu/kT)}}\right]$$

Einstein's Model of a Crystal

$$U = \frac{3}{2}N_0\hbar\nu\left[\frac{1 + e^{-(\hbar\nu/kT)}}{1 - e^{-(\hbar\nu/kT)}}\right]$$

Derive Heat Capacity (C_v).

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = 3N_0 k\left(\frac{\hbar\nu}{kT}\right)^2 \frac{e^{-(\hbar\nu/kT)}}{\left(1 - e^{-(\hbar\nu/kT)}\right)^2}$$

$$C_v = 3R \left(\frac{\hbar\nu}{kT}\right)^2 \frac{e^{-(\hbar\nu/kT)}}{\left(1 - e^{-(\hbar\nu/kT)}\right)^2} = 3R \left(\frac{\hbar\nu}{kT}\right)^2 \frac{e^{\hbar\nu/kT}}{\left(e^{\hbar\nu/kT} - 1\right)^2}$$

$$\theta = \frac{\hbar\nu}{k} \qquad C_v = 3R \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}$$

$$u = \frac{\theta}{T} \qquad C_v = 3R \frac{u^2 e^u}{\left(e^u - 1\right)^2}$$

at $T > \theta \rightarrow C_v = 3R$ per mole
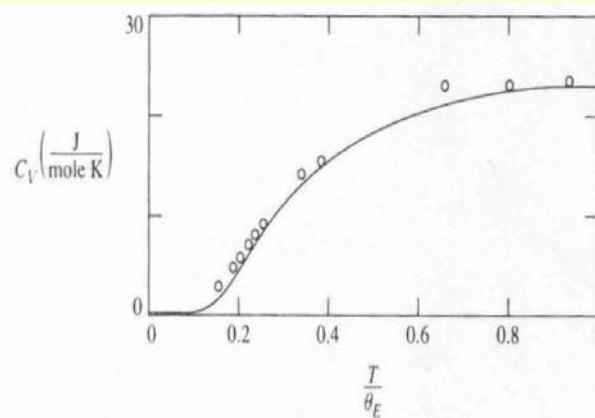
(Dulong Petit's law)

FIGURE 6.3

Comparison of experimentally measured heat capacity for diamond with that computed from the Einstein one parameter model. $\theta_E = (\hbar\nu/k)1320$ K. Figure from C. Kittel, *Introductin to Solid State Physics*, 4th ed. John Wiley, New York, NY (1971)

C_v = 3R   per mole   = 24.94 J/mole
(Dulong Petit's law)

Copper   0.386 J/gm °C x 63.6 gm/mole = 24.6 J/mol °C
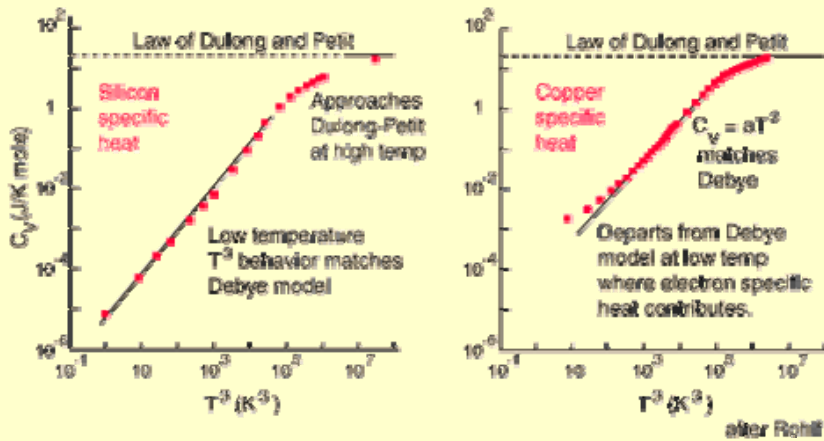Lead   0.128 J/gm °C x 207 gm/mole = 26.5 J/mol °C

$$u = \frac{\theta}{T} \qquad C_v = 3R\,\frac{u^2 e^u}{\left(1 - e^u\right)^2}$$

Debye : frequency distribution

$$u = \frac{\theta_D}{T} \qquad C_v = 3R\left[\frac{12}{u^3}\int_0^u \frac{x^3}{e^x - 1}\,dx - \frac{3u}{e^u - 1}\right]$$

θ_D = Debye temperature

Departure from the Law of Dulong and Petit

http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html

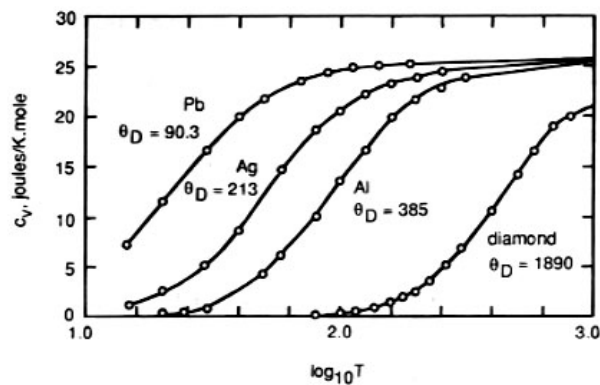**Figure 6.3** The constant volume molar heat capacities of several solid elements. The curves are the Debye equation with the indicated values of θ_D.

Gaskell

Monatomic Gas Model (only translational K.E.)

gas in a box of $l_x \times l_y \times l_z$

position : $\vec{x} = (x, y, z)$

velocity : $\vec{v} = (v_x, v_y, v_z)$

What is partition function?

$$P \equiv \sum_{i=1}^{r} e^{-(\varepsilon_i / kT)} \qquad \varepsilon = ?$$

$$\varepsilon = \frac{1}{2} mv^2 = \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right)$$

$$P \equiv \sum_{i=1}^{r} e^{-(\varepsilon_i / kT)} \qquad \varepsilon = \frac{1}{2} mv^2 = \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right)$$

$$P = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(\varepsilon / kT)} dv_x dv_y dv_z dx dy dz$$

$$= \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-1/(2kT)m\left(v_x^2 + v_y^2 + v_z^2\right)} dv_x dv_y dv_z dx dy dz$$

$$= \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\left(mv_x^2 / 2kT\right)} e^{-\left(mv_y^2 / 2kT\right)} e^{-\left(mv_z^2 / 2kT\right)} dv_x dv_y dv_z dx dy dz$$

$$= \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} dx dy dz \int_{-\infty}^{\infty} e^{-\left(mv_x^2 / 2kT\right)} dv_x \int_{-\infty}^{\infty} e^{-\left(mv_y^2 / 2kT\right)} dv_y \int_{-\infty}^{\infty} e^{-\left(mv_z^2 / 2kT\right)} dv_z$$

$$V = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} dx dy dz$$

$$\int_{-\infty}^{\infty} e^{-a^2 x^2}\, dx = \frac{\sqrt{\pi}}{a}, \qquad a^2 = m/2kT \qquad \int_{-\infty}^{\infty} e^{-(m/2kT)v^2}\, dv = \sqrt{\frac{2\pi kT}{m}}$$

∴ The partition function for a monatomic ideal gas is

$$P = V\left[\frac{2\pi kT}{m}\right]^{3/2}$$

$$\ln P = \ln\left[V\left(\frac{2\pi kT}{m}\right)^{3/2}\right] = \ln V + \frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) + \frac{3}{2}\ln T$$

$$\left(\frac{\partial \ln P}{\partial T}\right)_V = \frac{3}{2}\frac{1}{T}$$

$$P = V\left[\frac{2\pi kT}{m}\right]^{3/2} \qquad \left(\frac{\partial \ln P}{\partial T}\right)_V = \frac{3}{2}\frac{1}{T}$$

Derive Helmholz free energy.

$$F = -N_0 kT \ln P = -N_0 kT \ln\left[V\left(\frac{2\pi kT}{m}\right)^{3/2}\right]$$

Derive Entropy.

$$S = N_0 k \ln P + N_0 kT \left(\frac{\partial \ln P}{\partial T} \right)_v$$

$$= N_0 k \ln \left[V \left(\frac{2\pi kT}{m} \right)^{3/2} \right] + N_0 kT \left(\frac{3}{2T} \right)$$

$$S = N_0 k \ln \left[V \left(\frac{2\pi kT}{m} \right)^{3/2} \right] + \frac{3}{2} N_0 k$$

Derive internal energy.

$$U = N_0 kT^2 \left(\frac{\partial \ln P}{\partial T} \right)_v = N_0 kT^2 \left(\frac{3}{2} \frac{1}{T} \right) = \frac{3}{2} N_0 kT$$

$$\text{or} \quad U = F + TS = \frac{3}{2} N_0 kT$$

What is C_v ?

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = \frac{3}{2} N_0 k = \frac{3}{2} R$$

for one mole of the gas

Derive pressure.

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial\left(-N_0 kT \ln P\right)}{\partial V}\right)_T = N_0 kT \left(\frac{\partial \ln P}{\partial V}\right)_T$$

$$= N_0 kT \left[\frac{\partial}{\partial V}\left(\ln V + \frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) + \frac{3}{2}\ln T\right)\right]_T$$

$$P = N_0 kT \frac{1}{V} \qquad\qquad PV = N_0 kT = RT$$

Assumption: The energy of each atom is contained
in its translational kinetic energy.

Molecules of two or more atoms (H_2, CO_2, CH_4, etc)
Rotational and vibrational K.E. should also be considered.

Kinetic energies of rotation and vibration has
the same mathematical form as translation energy.

In rotational kinetic energy, moment of inertia and
angular velocity are replaced for mass and
translational velocity, respectively.

$$\varepsilon = \sum_{j=1}^{n} b_j v_j^2$$

$$P = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} dx\,dy\,dz \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-(1/kT)\sum b_j v_j^2} dv_1 dv_2 \ldots dv_n$$

$$= V \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \prod_{j=1}^{n} \left[e^{(-b_j/kT)v_j^2} \right] dv_1 dv_2 \ldots dv_n$$

$$\int_{-\infty}^{\infty} e^{-a^2 x^2} dx = \frac{\sqrt{\pi}}{a}, \quad \text{where } a^2 = b_j / kT$$

$$\int_{-\infty}^{\infty} e^{(-b_j/kT)v_j^2} dv_j = \left[\frac{\pi kT}{b_j} \right]^{1/2}$$

$$P = V \prod_{j=1}^{n} \left[\frac{\pi kT}{b_j} \right]^{1/2}$$

$$\ln P = \ln V + \sum_{j=1}^{n} \ln \left(\frac{\pi kT}{b_j} \right)^{1/2}$$

$$\ln P = \ln V + \sum_{j=1}^{n} \frac{1}{2} \ln \left(\frac{\pi k}{b_j} \right) + \sum_{j=1}^{n} \frac{1}{2} \ln T$$

$$\left(\frac{\partial \ln P}{\partial T} \right)_V = 0 + 0 + \sum_{j=1}^{n} \frac{1}{2} \frac{1}{T} = \frac{n}{2T}$$

Derive C_v.

$$U = N_0 kT^2 \left(\frac{\partial \ln P}{\partial T} \right)_v = N_0 kT^2 \frac{n}{2T}$$

$$U = n \cdot \frac{1}{2} N_0 kT = N_0 \cdot n \cdot \frac{1}{2} kT$$

$$C_v = n \cdot \frac{1}{2} N_0 k = N_0 \cdot n \cdot \frac{1}{2} k = n \cdot \frac{R}{2}$$

Each independent component of motion of the molecules in the gas contributes the same quantity, $\frac{1}{2} kT \rightarrow \frac{1}{2} RT$ per mole

$\rightarrow$ Principle of equipartition of energy

Diatomic molecule
- 3 translational degrees of freedom (x, y, z)
- 2 rotational degrees of freedom (θ, ϕ)
- 1 vibrational degrees of freedom
  (r: internuclear distance,
  $\frac{1}{2}$ kT for K.E. $\frac{1}{2}$ kT for P.E.)

$\rightarrow$ U = 7/2 kT, C_v = 7/2 R, Cp = 9/2 R

TABLE 6.2
Comparison of heat capacities of monotonic and diatomic gases with values predicted from the principle of equipartition of energy

$C_p = 9/2\ R$

Monatomic gas	C_P (J/mole-K)	Diatomic gas	C_P (J/mole-K)
Ideal Gas	$5/2R = 20.79$	Ideal Gas	$7/2 = 29.10$
Argon	20.72	Chlorine (Cl_2)	33.82
Krypton	20.69	Fluorine (F_2)	31.32
Neon	20.76	Hydrogen (H_2)	28.76
Radon	20.81	Oxygen (O_2)	29.32
Xenon	20.76	Nitrogen (N_2)	29.18

What is Heat Capacity?
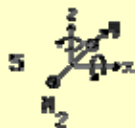
→ *capacity to store energy (heat)*

Degrees of freedom

3

Monoatomic

$C_v = \frac{3}{2}R = 12.5\ \dfrac{J}{mol\ K}$

Helium   12.5
Argon   12.6

5

Diatomic

$C_v = \frac{5}{2}R = 20.8\ \dfrac{J}{mol\ K}$

Nitrogen (N_2)   20.7
Oxygen (O_2)   20.8

$C_V = 7/2\ R$

6

Polyatomic

$C_v = \frac{6}{2}R = 24.9\ \dfrac{J}{mol\ K}$

Ammonia (NH_4)   29.0
Carbon dioxide (CO_2)   29.7

$C_V > 7/2\ R$

http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html

In real diatomic molecule, $C_v \neq 7/2\,R$ Why?

The vibrational contribution of a diatomic molecule can be analyzed through the model of an harmonic oscillator (Einstein's model).
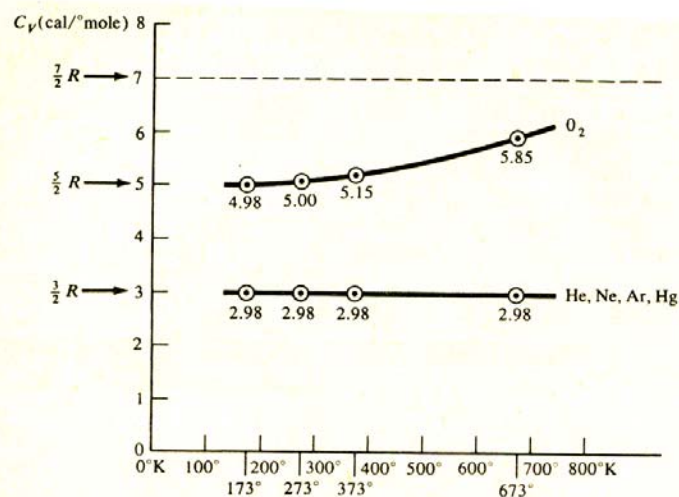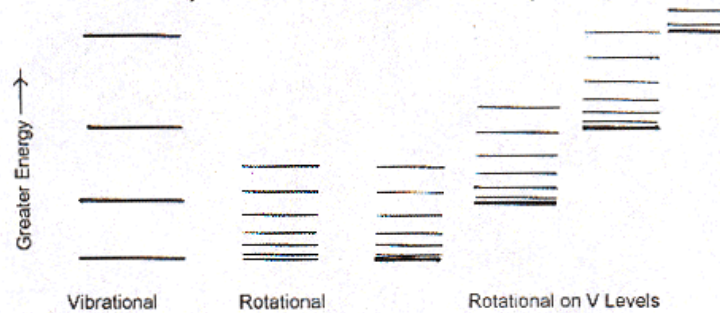

FIGURE 2-21. *The measured heat capacities for most monatomic gases agree well with their expected values of $\frac{3}{2}R$. But those even for diatomic molecules such as O_2 deviate widely from the predicted value of $\frac{7}{2}R$, and the deviation is worse at lower temperatures. For explanation, see text.*

R.E. Dickerson (1969)
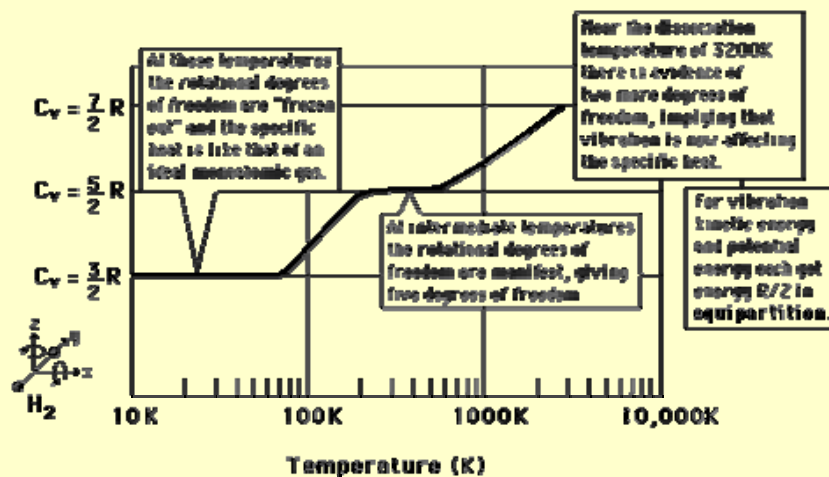
Quantized Energy → Energy Levels

Figure 2. Schematic of vibrational (V) and rotational (R) energy levels for complex molecules
(Molecules more complex than water can have varied conformations, allowing more V and R modes.)
Each V level has an R level that may overlap the next higher V level. Therefore, showing a complete schematic is confusing. The staggered diagram at the right should be "slid together" horizontally for a semi-realistic depiction.

The conclusion that can be drawn from this schematic is important: When more energy is put into a system, its molecules can occupy a great many additional energy levels – higher energy V levels that each can have many R levels (and of course every R level has translational levels within it).

Greater Energy →

Vibrational   Rotational   Rotational on V Levels

http://www.2ndlaw.com/entropy.html

Hydrogen Specific Heat

$C_v = \frac{7}{2} R$

$C_v = \frac{5}{2} R$

$C_v = \frac{3}{2} R$

At these temperatures the rotational degrees of freedom are "frozen out" and the specific heat is like that of an ideal monatomic gas.

At intermediate temperatures the rotational degrees of freedom are manifest, giving five degrees of freedom

Near the dissociation temperature of 3200K there is evidence of two more degrees of freedom, implying that vibration is now affecting the specific heat.

For vibration kinetic energy and potential energy each get energy R/2 in equipartition.

H_2

10K   100K   1000K   10,000K

Temperature (K)

http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html

For polyatomic molecules, vibrational contribution should be estimated. (Einstein model)

$h\nu = k\theta,$ θ : characteristic vibrational temperature

$$C_v^{vib} = R\left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2} \; ; \text{ approach R when } \frac{\theta}{T} \text{ goes to } \infty.$$

$$C_v^{vib} = R \frac{u^2 e^u}{\left(e^u - 1\right)^2} \; ; \qquad u = \frac{h\nu}{kT} = \frac{\theta}{T}$$

Gases with linear molecules
- 3 translational degrees of freedom
- 2 rotational degrees of freedom
- 3n – 5 vibrational contributions

$$C_v = R\left[\frac{5}{2} + \sum_{i=1}^{3n-5} \frac{u_i^2 e^{u_i}}{\left(e^{u_i} - 1\right)^2}\right]$$

Gases with non-linear molecules
   - 3 translational degrees of freedom
   - 3 rotational degrees of freedom
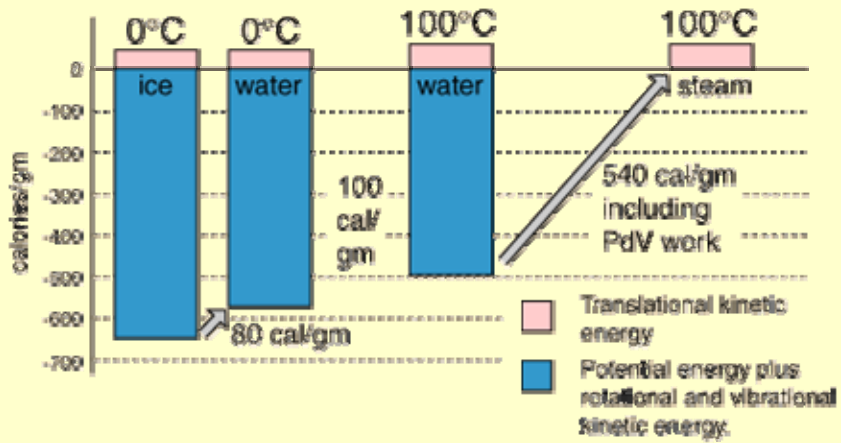   - 3n – 6 vibrational contributions

$$C_v = R\left[3 + \sum_{i=1}^{3n-6} \frac{u_i^2 e^{u_i}}{\left(e^{u_i} - 1\right)^2}\right]$$

Phase changes
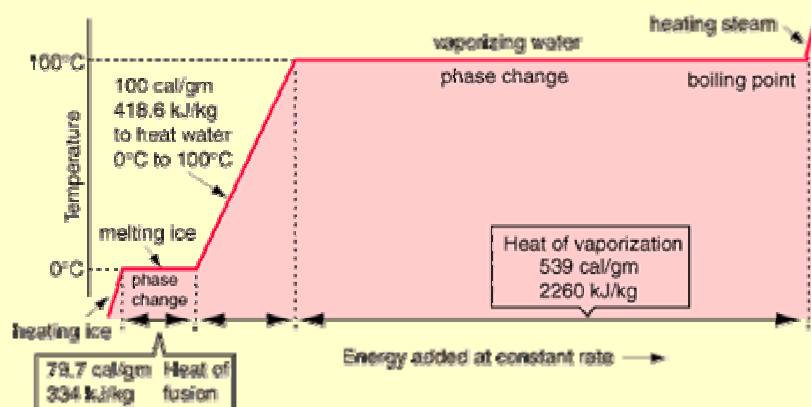
Energy Involved in the Phase Changes of Water

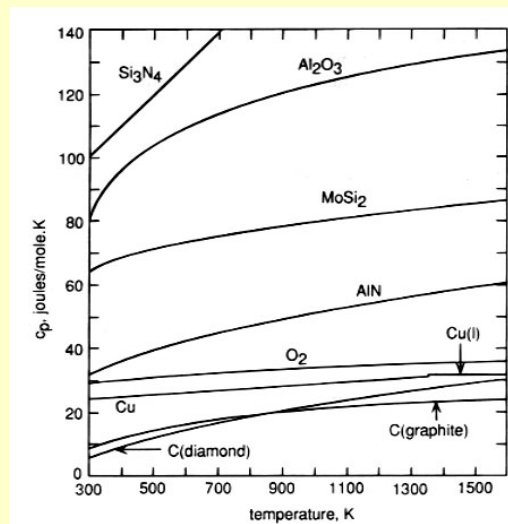http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html

Figure 6.4 The variations, with temperature, of the constant-pressure heat capacities of several elements and compounds.
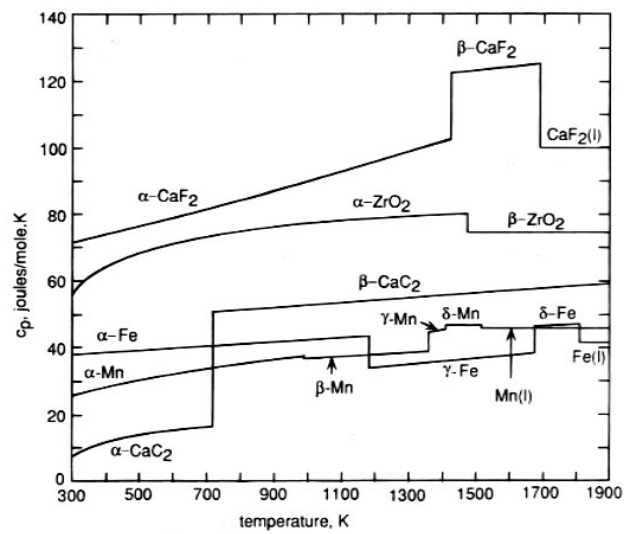
Figure 6.5 The variations, with temperature, of the constant-pressure molar heat capacities of some elements which exhibit allotropy and some compounds which exhibit polymorphism.