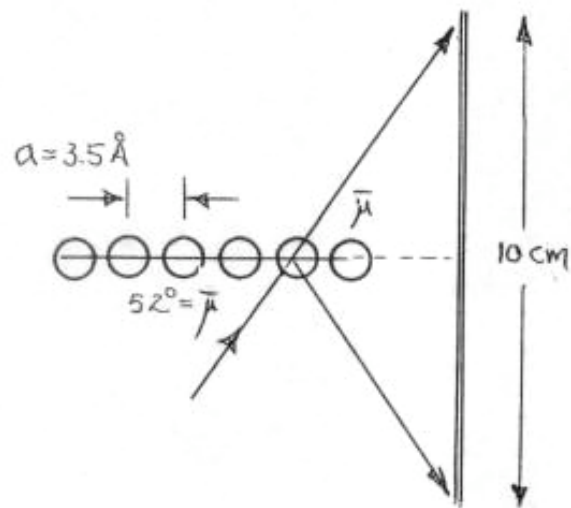


Graded problems:

1. **Planes and directions.** Consider a 2-dimensional lattice defined by translations T_1 and T_2 .
 - a. Is the direction $[hk]$ perpendicular to the plane (hk) ? Always? Sometimes? Never?
 - b. Let's now extend our consideration to three-dimensional lattices. Is the direction $[hkl]$ perpendicular to the plane (hkl) ?

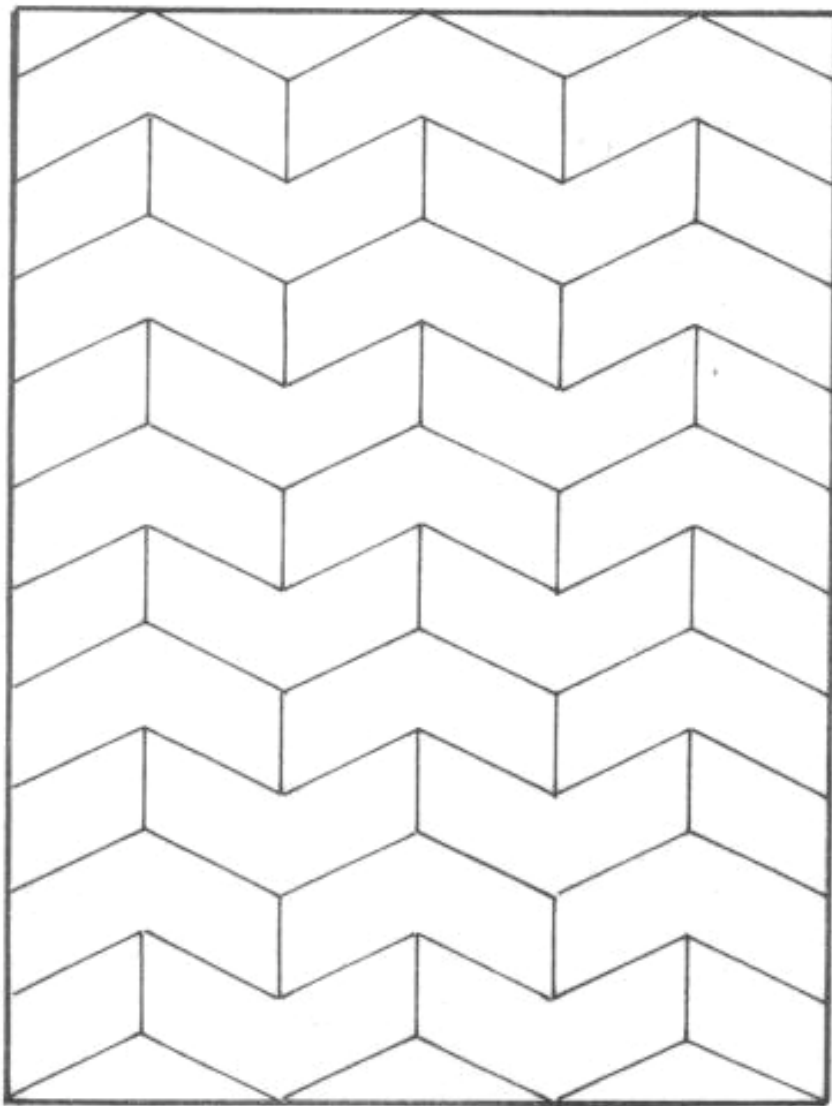
2. **Assignment of Miller-Bravais indices.** The following process leads to unambiguous determination of the Miller-Bravais indices (hkl) for a rational lattice plane in terms of its intercepts (in units of a , b , and c) on the edges of the unit cell. The method is based on the fact that the intercepts of the first plane from the origin are $1/h$ $1/k$ $1/l$ and those of the n^{th} plane from the origin are n/h n/k n/l . Therefore, for any rational plane in the stack one can: (a) find n/h n/k n/l ; (b) take the reciprocals h/n k/n l/n ; (c) clear the common factor $1/n$ to obtain hkl . The indices hkl , therefore, should contain no common factor. However, one often sees diffraction patterns with peaks indexed in terms of the indices of the d_{hkl} that gave rise to them. Some of these are assigned indices such as 222, 400, or 550 (to name a few) that obviously contain a common factor. What's going on here? Don't these people know how to assign Miller-Bravais indices properly? Please provide an explanation of this situation using Bragg's law.

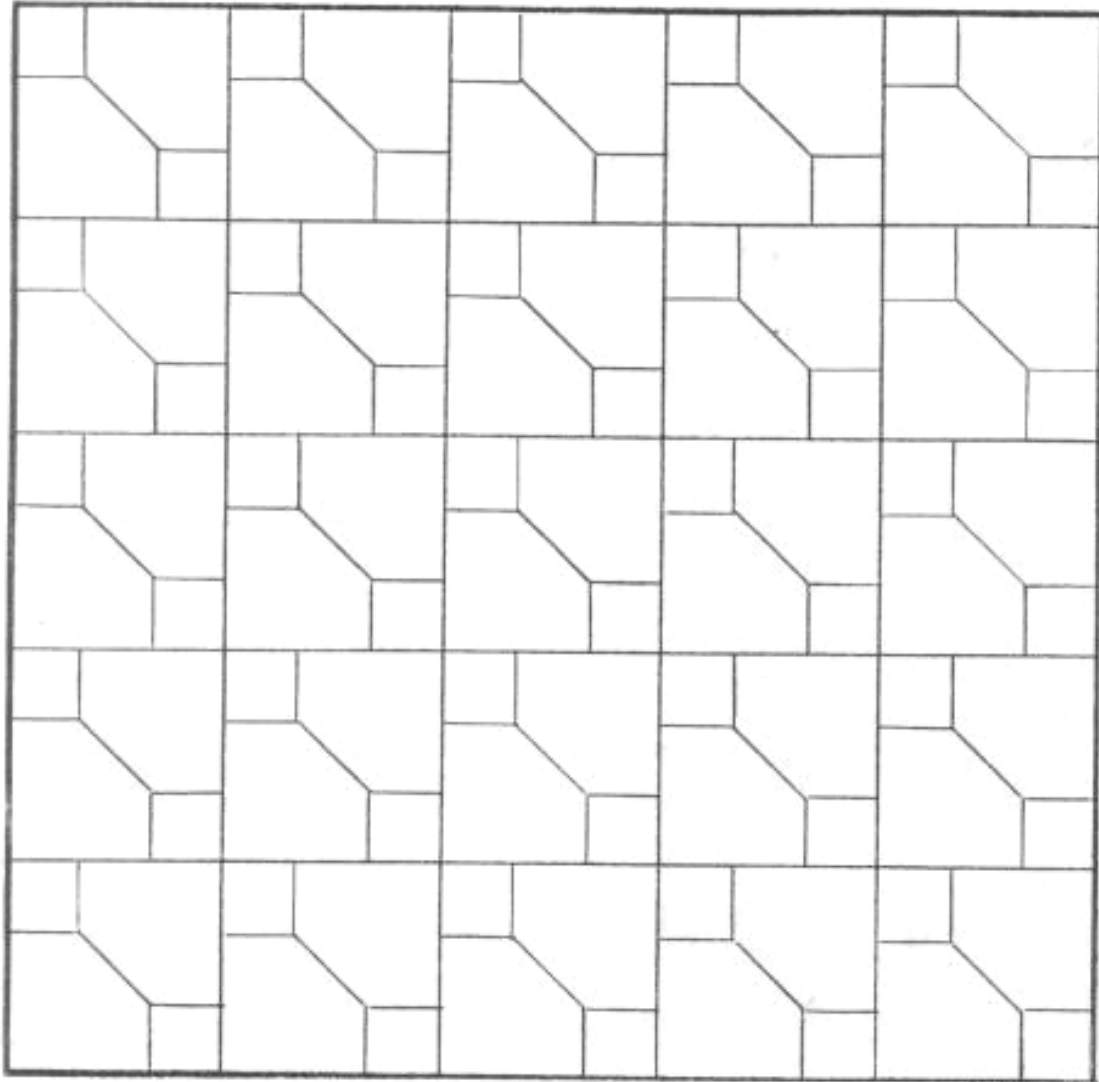
3. **1D diffraction.** We direct a beam of X-radiation with wavelength $\lambda = 1 \text{ \AA}$ at an angle of incidence $\theta = 52^\circ$ onto a 'real' one-dimensional crystal consisting of a row of identical atoms spaced at a lattice constant $a = 3.5 \text{ \AA}$. A $10 \times 10 \text{ cm}$ square piece of film is placed in an orientation normal to the lattice row (see sketch of the arrangement below).
 - a. At what distance from the crystal must the film be placed if a record of the complete diffraction cone is to be recorded on the film?
 - b. Sketch qualitatively (but realistically) the distribution of intensity that you would expect to see on the film, remembering that the electrons scattering the radiation have a spatial distribution about the atom that is comparable to 1 \AA (with a lattice constant of 3.5 \AA , the atomic radius will be 1.75 \AA).
 - c. Will a record of any other diffraction cone appear on the film?



4. **Identifying symmetries.** Two patterns follow that are translationally-periodic and which possess symmetry elements of various sorts.

- Draw on the patterns a set of dots that represent lattice points (bold, plump little dots, please, so that they may be readily discerned by a grader!). Connect four of them to define a cell.
- Draw in, using standard symbols (bold lines for mirror lines, n-gons for rotation axes), the loci of all symmetry elements that you can find. (Note: As everything is repeated by translation you need do this only at the periphery and within the area encompassed by one unit cell).
- Identify with shading the asymmetric unit- that minimal area of the pattern which, upon specification of the symmetry of the pattern, would permit generation of the entire pattern.





5. **Interpretation of the second law.** Mortimer problem 4.46, parts a-f.

6. **The free energy of a rubber band.** If a rubber band is stretched adiabatically, its temperature increases (try it! Stretch a rubber band and press it immediately against your lip). If we assume the rubber band maintains a constant volume (though its shape changes), we can write its fundamental equation as:

$$dU = TdS + (kl)dl$$

...where k is an elastic constant for stretching the band (equivalent to the elastic constant of a spring), and l is the length of the rubber band. Measurements show the elastic constant k is always positive and increases with increasing temperature.

(a) Derive the Helmholtz free energy for the rubber band at constant volume.

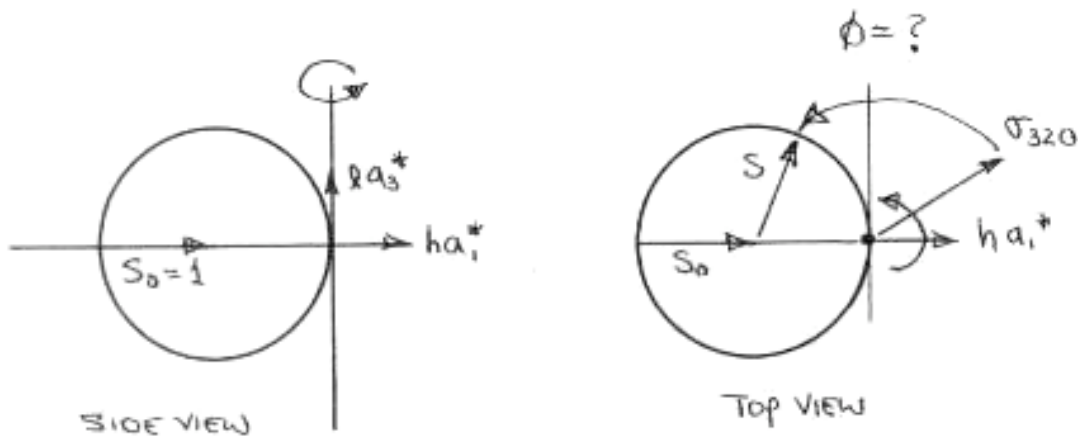
(b) Derive the Maxwell relation for this material from the Helmholtz free energy and use it to predict whether the entropy increases, decreases, or stays the same when the rubber band is stretched *isothermally*.

(c) If the rubber band is stretched adiabatically, does the internal energy increase, decrease, or stay the same? (Show why).

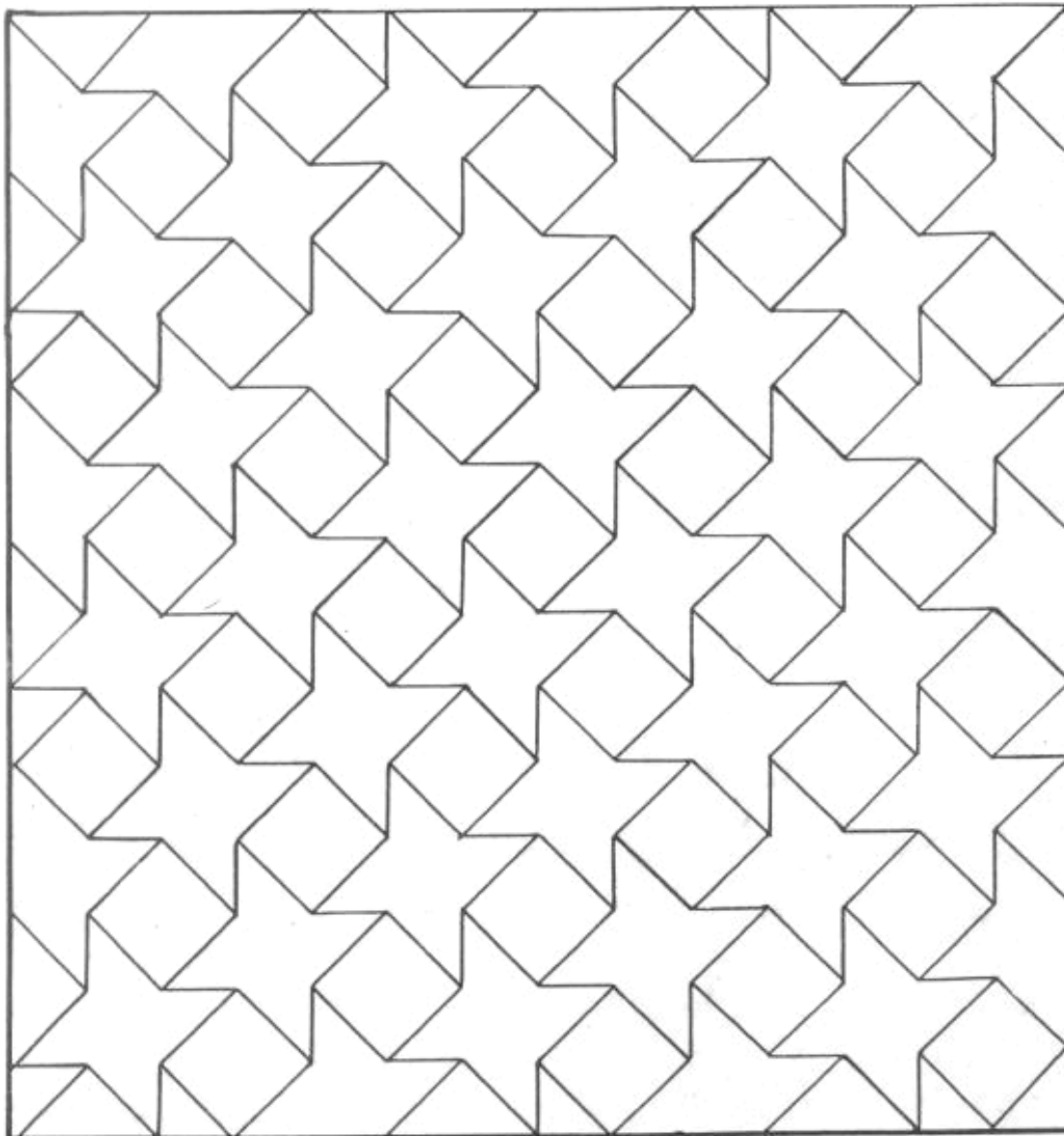
Optional problems:

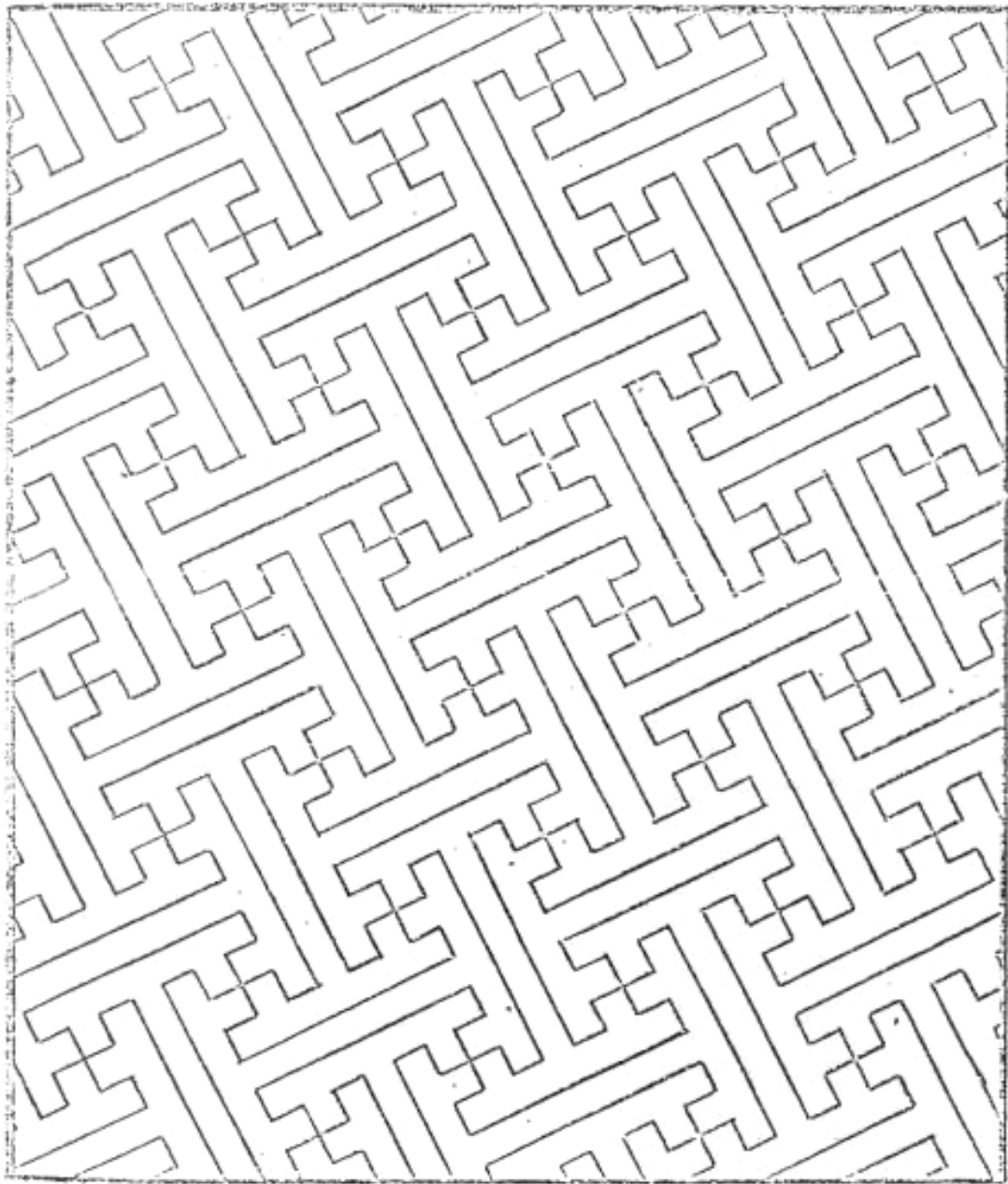
7. A crystal that is cubic, with lattice constant $a = 10 \text{ \AA}$ is irradiated with Cu K α radiation ($\lambda_{\text{Cu K}\alpha} = 1.54178 \text{ \AA}$). A side-view of the experiment and the sphere of reflection that is employed in the Ewald Construction to interpret the experiment is shown below. The vectors that are used to describe the reciprocal lattice are $a_1^* = \lambda/d_{100} = \lambda/a_1$, $a_2^* = \lambda/a_2$, and $a_3^* = \lambda/a_3$. The reciprocal lattice vectors are parallel to the directions of the corresponding a_1 , a_2 , and a_3 . The reciprocal lattice vector \vec{g}_{hkl} that must be brought onto the surface of the sphere of reflection to generate diffraction by d_{hkl} is given by $\vec{g}_{hkl} = ha_1^* + ka_2^* + la_3^*$. The crystal is rotated about an axis normal to the incident beam to satisfy the diffraction condition. a_3^* is oriented along the rotation axis and a_1^* is initially parallel to \vec{S}_0 , the direction of the incident beam.

- What is the maximum value of l for which a diffraction peak can be generated?
- What is the maximum value of h for which a peak will be generated?
- What is the total number of different diffraction peaks of the class $hk0$ that will be generated as the crystal is rotated through 360° ? ($\pm h \pm k$ and $\pm l$ are to be considered 'different' indices).
- Through what angle in a counter-clockwise direction must the crystal be rotated in order to generate the 320 diffraction peak?



8. **More practice with symmetry recognition.** Repeat problem 4 for the two (more difficult) periodic patterns provided below.





9. **The second law applied to heating processes.**

- a. One kg of water at 273K is brought into contact with a heat reservoir at 373K. When the water has reached 373K, what is the entropy change of the water, of the heat reservoir, and of the universe?
- b. If the water had been heated from 273K to 373K by first bringing it into contact with a reservoir at 323K and then with a reservoir at 373K, what would have been the entropy change of the universe?
- c. Explain how the water might be heated from 273K to 373K with almost no change of entropy of the universe.

The heat capacity of water can be taken as: $C_p^L = 75.31 \text{ J/mole K}$

10. **Gibbs free energy and Helmholtz free energy at equilibrium.** Mortimer problem 5.45.

11. **The equivalence of maximizing entropy and minimizing internal energy.** A pair of blocks initially at different temperatures are placed in thermal contact. The blocks have constant total volume. Using an analysis similar to our entropy-based calculations in class, show that if the total entropy of the blocks A and B is held constant, then $dU_{total} = 0$ at equilibrium will require $T_A = T_B$ at equilibrium.

12. **Identifying stable phases.** You are given below measured enthalpy and entropy data taken at 1 atm pressure as a function of temperature for two different phases (A and B) of a new material. Only one of these phases is the equilibrium phase at any given temperature, the other is metastable.

- a. At $T = 350\text{K}$, which phase is stable, and which is metastable?
- b. Show why the metastable phase will be driven to spontaneously transform to the stable phase at this temperature.

Data: $H^A = 5.91(T - 298) + 2.9 \times 10^{-3}(T^2 - 298^2)$ cal/mole
 $S^A = 13.2 + 5.91 \log(T/298) + 2.9 \times 10^{-3}(T - 298)$ cal/mole K

$$H^B = 1568 + 5.21(T - 395) + 3.525 \times 10^{-3}(T^2 - 395^2)$$
$$S^B = 16.22 + 5.21 \log(T/395) - 3.525 \times 10^{-3}(T - 395)$$
 cal/mole K