

Fundamental Principles and Equations for a Closed SystemRef: C H P Lupis, Chemical Thermodynamics of Materials, North-Holland, 1983, Chapter I.**Lecture 3****2. The Second Law of Thermodynamics for Closed System****2.1 Enunciation of the second law**

Under a given set of conditions, a system can be imagined to undergo many processes for which the energy is conserved (the first law). But in practice, only those processes occur in which the system goes to its state of rest, i.e., to a state of equilibrium.

By considering that this “state of equilibrium” is a property of the system, and that this property can be described by a function, the Second Law determines the direction and extent of such processes. The law affirms the existence of a state function named *entropy*, which tends to increase for all processes if the system is remained to be isolated during the whole process.

For all *reversible* processes, the state function entropy, S , is defined by

$$dS = \frac{\delta Q_{rev}}{T} \quad (2.1)$$

And for all *irreversible* processes

$$dS > \frac{\delta Q}{T} \quad (2.2)$$

It may be noted that, for an isolated system, heat transfer across the boundary is zero and thus, the entropy of system in isolated condition always tend to increase.

Proof of Second Law

Consider a cylinder of two compartments of volume V_1 and V_2 .

In one process, compartment 1 was filled with an ideal gas. By opening the connection between the compartments the gas is allowed to expand irreversibly to occupy total volume V_1+V_2 . Since the system is isolated, energy remains constant, and as the energy of ideal gas is a function of temperature only, the temperature of the system also remains constant. Now we want to calculate the entropy change for this irreversible process.

We imagine a frictionless piston which restores the gas to its original position in a reversible manner and with the interaction with the surroundings. The energy remains the same as before because it is a state function. Consequently,

$$Q_{rev} = -W_{rev,T} = \int_{V_1+V_2}^{V_1} P dV = nRT \ln\left(\frac{V_1}{V_1 + V_2}\right)$$

and

$$S_1 - S_2 = \frac{Q_{rev}}{T} = nR \ln\left(\frac{V_1}{V_1 + V_2}\right)$$

Thus the entropy change in the original irreversible process is

$$S_2 - S_1 = \frac{Q_{irr}}{T} = nR \ln\left(\frac{V_1 + V_2}{V_1}\right)$$

which is positive.

2.2 Entropy as a measure of reversibility and degradation

If the system remained isolated,

for a reversible process, $\Delta S = 0$

for an irreversible process, $\Delta S > 0$

So entropy provides a measure of the degree of irreversibility of a transformation, or a measure of the degree of degradation of the system experiencing this irreversible transformation.

The degree of irreversibility caused during a spontaneous process is due to the degradation of energy due to friction, etc. The higher the irreversibility, the higher is the degradation.

2.3 Criteria of equilibrium

For all irreversible processes, according to the second law,

$$dS > \frac{\delta Q}{T} \quad \text{or} \quad TdS > \delta Q \quad (2.2)$$

This inequality of the second law may take several forms. Using the first law, this equation becomes

$$TdS > dE - \delta W \quad (2.3)$$

Using only the mechanical work interactions, for all irreversible processes, we have

$$dE - TdS + PdV < 0 \quad (2.4)$$

The thermodynamic criterion of equilibrium for a closed system where no irreversible change occurs may be expressed as

$$dS \leq \frac{\delta Q}{T} \quad \text{or} \quad TdS \leq \delta Q \quad (2.5)$$

$$dE - TdS + PdV \geq 0 \quad (2.6)$$

When the process is reversible, the equality sign in Eq.(2.6) will prevail and yield

$$dE = TdS - PdV \quad (2.7)$$

Equation (2.7) can be equally applied to irreversible processes since energy is a function of state only.

Depending on the restrictions to which a system is subjected, introduction of other thermodynamic function is often useful.

(1) At constant S and P

$$(dE - TdS + PdV)_{S,P} \geq 0$$

$$(dE + PdV)_{S,P} \geq 0$$

$$dH_{S,P} \geq 0$$

$$H = E + PV$$

$$dH = dE + PdV + VdP$$

$$dE + PdV = dH - VdP$$

$$(dE + PdV)_{S,P} = dH_{S,P}$$

(2) At constant T and V

$$(dE - TdS + PdV)_{S,P} \geq 0$$

$$(dE - TdS)_{T,V} \geq 0$$

$$dA_{T,V} \geq 0$$

A = Helmholtz free energy (used as F in UG classes)

$$A = E - TS$$

$$dA = dE - TdS - SdT$$

$$(dE - TdS)_{T,V} = dA_{T,V}$$

(3) At constant T and P

$$(dE - TdS + PdV)_{T,P} \geq 0$$

$$dG_{T,P} \geq 0$$

$$G = H - TS = (E + PV) - TS$$

$$dG = dE + PdV + VdP - TdS - SdT$$

$$dE - TdS + PdV = dG - VdP + SdT$$

$$(dE - TdS + PdV)_{T,P} = dG_{T,P}$$

This means that at constant T and P, the equilibrium state has the minimum free energy and a spontaneous transformation can only occur if it is associated with a decrease in the Gibbs free energy of the system.

3. The Third Law of Thermodynamics

3.1 Enunciation of the Third Law

In 1902 TW Richards found that, as the temperature is decreased, the free energy of a reaction approaches asymptotically its enthalpy change:

$$\Delta G = \Delta H - T\Delta S$$

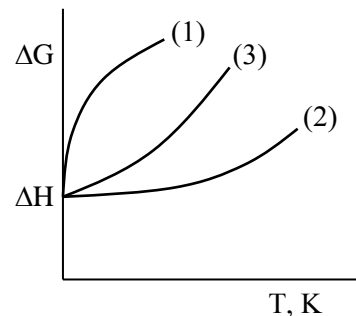
$$\text{Slope, } -\Delta S = \left(\frac{\partial \Delta G}{\partial T}\right)_P$$

When $T \rightarrow 0 \text{ K}$, $\Delta G \rightarrow \Delta H$.

So Richards proclaimed that ΔS and ΔC_p approach zero as T is decreased.

But when ΔG is plotted against T, we can see that ΔG may approach ΔH with a

- (1) vertical slope,
- (2) a horizontal slope, and
- (3) an oblique slope.



- (1) systems not obeying the 3rd law
- (2) perfect crystal
- (3) disordered crystals

Using Richard's experimental data, Nernst found that the slope was never vertical and could be horizontal and suggested that at 0 K the entropy increment of reversible reactions among perfect crystalline solids is zero.

Plank generalised this principle and subsequently developed the third law:

"Entropies of all perfect crystalline solids at 0 K are zero."

However a better statement of the third law was given by Lewis and Randaall:

"If the entropy of each element in some "perfect" crystalline state is taken as zero at the absolute zero of temperature, every substance has a finite entropy: but at the absolute zero of temperature the entropy may become zero, and does so become in the case of "perfect" crystalline substances."

Here the word perfect not only means without defects such as vacancies or dislocations, but also without disorder in the arrangement of atoms. So the substance should be homogeneous and in complete internal equilibrium.

To be more rigorous, the statement of Lewis and Randall should include not only perfect crystalline substance at 0 K, but also "substances in any state in true thermodynamic equilibrium at 0 K (and consequently without defect)". A case in point would be liquid helium at 0 K.

An interesting alternate statement of the third law is that "the absolute zero of temperature can never be attained."

3.2 Consequence of the Third Law

Entropy increase due to rise in temperature at constant pressure is

$$S_T - S_{0K} = S_T = \int_0^T \frac{C_P}{T} dT \quad (3.1)$$

Similarly at constant volume

$$S_T = \int_0^T \frac{C_V}{T} dT \quad (3.2)$$

Moreover, because of the third law, the entropy must remain finite above 0 K. Thus, C_P/T or C_V/T in above two equations must also remain finite as T approaches to 0 K.

Now, according to the third law, the entropy of a perfect substance at 0 K is zero regardless of the pressure. Thus

$$\left(\frac{\partial S}{\partial P}\right)_{T=0K} = 0 \quad (3.3)$$

Using Maxwell's relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha = 0 \quad (3.4)$$

and thus

$$\alpha_{0K} = 0 \quad (3.5)$$

Experimentally, the coefficient of thermal expansion has indeed found to approach zero near 0 K.

The independence of entropy on the volume at 0 K leads to

$$\left(\frac{\partial S}{\partial V}\right)_{T \rightarrow 0K} = 0 \quad (3.6)$$

and since

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha}{\beta} \quad (3.7)$$

we obtain

$$\left(\frac{\alpha}{\beta}\right)_{0K} = 0 \quad (3.8)$$

As suggested by Eq.(3.8) and contrary to the behaviour of the coefficient of thermal expansion, there is no evidence that the coefficient of compressibility approaches zero at 0 K.

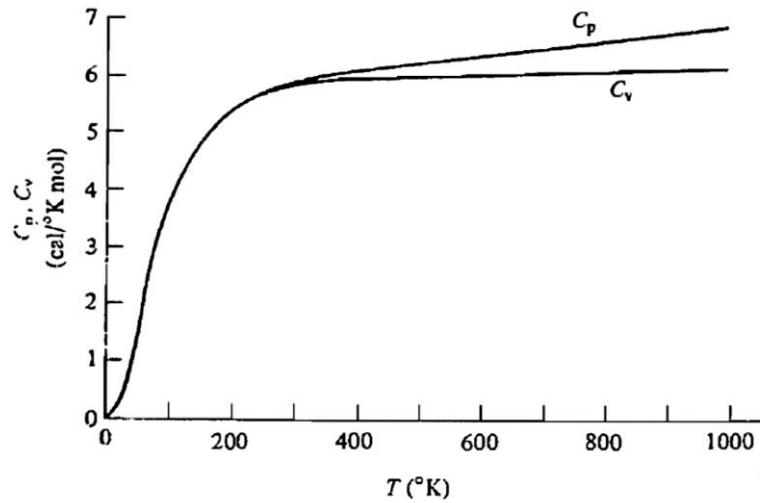
3.3 Measurement of Entropy

Temperature dependence of entropy at constant pressure:

$$\delta Q_P = TdS_P = C_P dT$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} > 0$$

Thus, for any phase the curve must always increase because its slope is always positive.



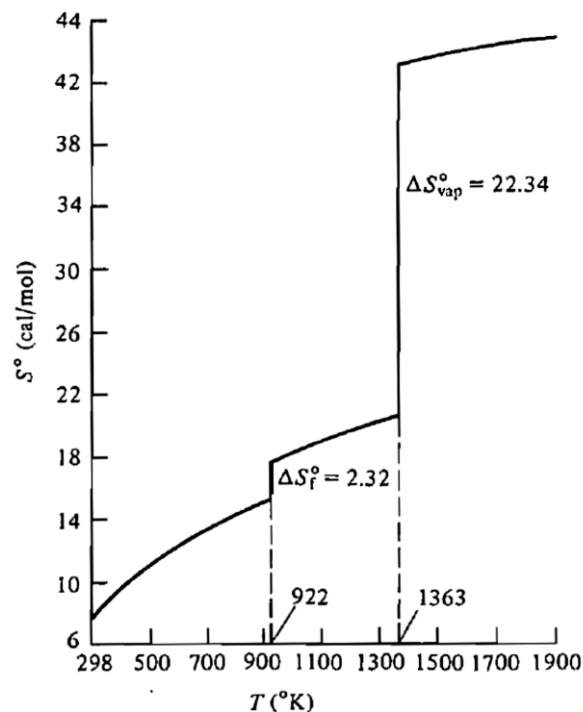
Temperature dependence of the heat capacities of copper at constant pressure and at constant volume..

There are discontinuities in the value of the function at temperatures of phase transformations such as melting or boiling.

For most metals

$$\Delta S_f^0 \approx 2 - 3 \text{ cal/mol K (Richard's rule)}$$

$$\Delta S_v^0 \approx 22 \text{ cal/mol K (Trouton's rule)}$$



Temperature dependence of the entropy of magnesium at 1 atm.

Better approximation for ΔS_f^0 is possible when entropy of fusion is correlated with the structure of solids. For example

$$\Delta S_f^0(\text{hcp}) - \Delta S_f^0(\text{fcc}) = \Delta S_f^0(\text{fcc}) - \Delta S_f^0(\text{bcc}) \approx 0.25 \text{ cal/mol K}$$

Other structures, e.g., rhombohedra, diamond cubic, or orthorhombic, are often associated with rather covalent or ionic character, not metallic one. Generally their entropies of fusion are significantly higher. For example, $\Delta S_f^0(\text{Sb, rh}) = 5.26$, $\Delta S_f^0(\text{Ge, dc}) = 7.3$, and $\Delta S_f^0(\text{Ga, or}) = 4.41$.

Under 1 atmospheric pressure and at room temperature (298 K), the entropy of a species may be obtained from

$$S_{298}^0 = \int_0^{298} C_p^0 d \ln T \quad (3.9)$$

At 298 K, C_p is generally very close to C_v (the difference, expressed as $C_p - C_v = TV\alpha^2/\beta$, is small) and Debye's model may be used to obtain an estimate of the entropy.

$$C_v = 464.6 \left(\frac{T}{\theta_D} \right)^3 \quad (3.10)$$

where θ_D is the *characteristic Debye temperature*. Thus a hard and light material such as carbon or silicon having a large vibrational characteristic temperature θ_D will have a relatively small S , while a soft and heavy material like mercury or lead having small θ_D will have a large S .

It is important to consider the relative magnitude of S_{298}^0 . Generally solid elements have entropies of less than 15 cal/g-at. K, and liquids are nearly in the same range (Richard's rule). Monatomic gases have entropies of the order of 30-40 cal/mol-K while diatomic gases have larger entropies, between 45-55 cal/mol-K (with notable exception of hydrogen because of its light weight and high θ_D). Triatomic and larger molecules have even larger entropies.

The entropies of solid and liquid compounds may be roughly estimates from the additions of the entropies of their constituent components in the solid or liquid states. So, a higher number of gram atoms per mol of a component correlate with a larger value for its entropy. For example, the values of ΔS_{298}^0 for Fe, $\text{Fe}_{0.95}\text{O}$, Fe_2O_3 , and Fe_3O_4 are, respectively, 6.52, 13.76, 20.89, and 34.72 cal/mol-K.

Entropies of reaction are defined in the same way as enthalpies of reaction, i.e., the entropy of the reaction

$$\nu_1 A_1 + \nu_2 A_2 + \dots + \nu_k A_k = \nu_{k+1} A_{k+1} + \dots + \nu_r A_r \quad \text{or,} \quad \sum_{i=1}^r \nu_i A_i = 0 \quad (3.11)$$

is

$$\Delta S = \sum_{i=1}^r \nu_i S_i \quad (3.12)$$

where S_i is the molar entropy of component A_i . Entropies of formation S_f of a compound have a definition similar to that of the enthalpies of formation.