MSE-204 Thermodynamics for Materials Science

L2. AUXILIARY FUNCTIONS & THEIR MEANING

FUNDAMENTAL EQUATION | AUXILIARY FUNCTIONS | EQUILIBRIUM | NATURAL VARIABLES | MAXWELL'S RELATIONS

Vaso Tileli | MXD 237

THE FUNDAMENTAL EQUATION OF STATE FOR A CLOSED SYSTEM

The basic equation for a closed system can be derived as follows. From the first law:

And for a reversible, quasi-static change we can substitute:

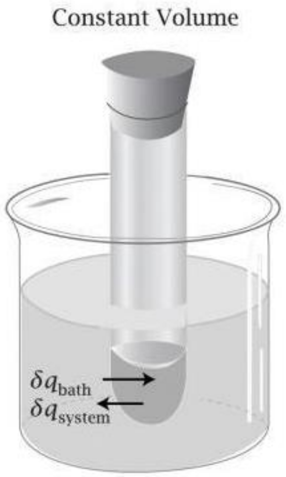
This equation is applicable ONLY when volume change is the only form of work. It is also applicable to closed systems which are in a state of internal equilibrium.
All of these quantities are state functions. Therefore, provided there is no irreversible changes in composition, if we go from an initial state A (p_A, T_A) to a final state B (p_B, T_B), the changes of S, U and V all have definite values, depending only on these states.

Finally for a cyclic process, we have:

The work performed in a reversible cycle may be obtained as an area on a p-V diagram or an area on a T-S diagram

DESCRIPTION OF THERMODYNAMIC SYSTEM

How many variables do you need in order to fully describe a thermodynamic system?



INTRODUCTION OF AUXILIARY FUNCTIONS

For many problems though there are functions that can be derived from these variables that are more convenient. These are:

1.

2.

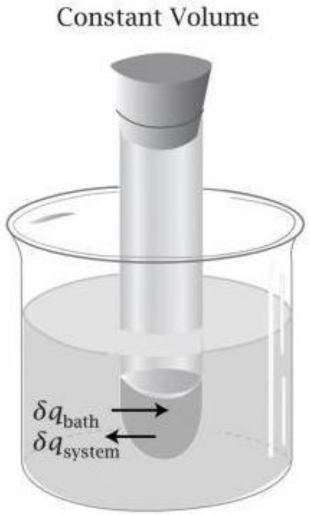
3.

These functions can be considered as Legendre transformations of the main variables.

More importantly, please note that <u>because all of the above functions are linear combinations of state functions, they are also state functions</u>. They are also extensive variables.

THE MEANING OF INTERNAL ENERGY DURING ISOCHORIC PROCESSES

First, we will look at an isochoric transformation:

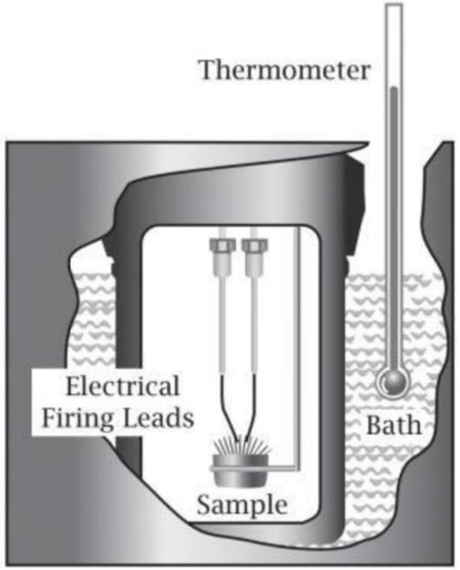


THE MEANING OF ENTHALPY DURING ISOBARIC PROCESSES

Let's look at an isobaric transformation:

MEASURABLE QUANTITIES IN THERMODYNAMICS:

HEAT CAPACITY



Heat capacity is an amount of heat required to raise the temperature of a system (or material) by 1 K. Alternatively, the heat uptake per unit temperature change is called the heat capacity.

You can measure an object's heat capacity in a calorimeter.
The heat capacity is the ratio of heat input to temperature change.

The instantaneous heat capacity, *C*, at the temperature *T* is the limiting value of the following ratio at the quantities q and ΔT become infinitesimal. Therefore, by definition:

$$C \equiv \frac{\delta q}{dT}$$

If follows that in order for the heat capacity to have a definite value, it must be specified that the heating is slow enough for the internal equilibrium to be achieved. Similarly, the measurement must always refer to a closed system.

Finally, the value of C remains indefinite until the path of heating is specified. This can be done by replacement of the heat through the first law. However, the mere statement that there is a temperature change in the system, as defined by the heat capacity, is insufficient to fix the values of dU or δw. Some other variable must be changed in a known manner or held constant.

MEASURABLE QUANTITIES IN THERMODYNAMICS:
HEAT CAPACITY AT CONSTANT VOLUME AND PRESSURE

For an **isochoric process** the heat capacity is:

$$dU = \delta q + \delta w = TdS - pdV$$

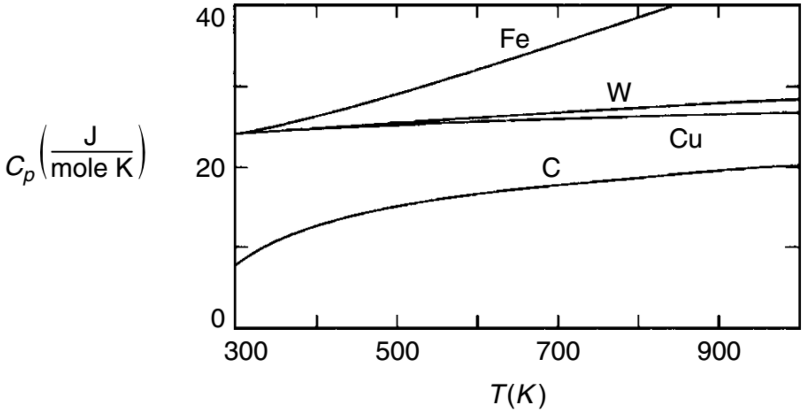
$$dV = 0$$

$$C_V = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$

Similarly, the heat capacity at **constant pressure** can be defined:

$$C_p = \left(\frac{\delta q}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p$$

And these are intensive properties of the system.



MEASURABLE QUANTITIES IN THERMODYNAMICS:
EXPANSIVITY AND ISOTHERMAL COMPRESSIBILITY COEFFICIENTS

These coefficients refer to fractional changes in volume $\frac{dV}{V}$ and are independent of the actual volume of the system.

The expansivity coefficient or coefficient of thermal expansion is defined:

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

The isothermal compressibility coefficient is defined:

$$\beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

And there are also intensive properties.

MEASURABLE QUANTITIES IN THERMODYNAMICS:
HEATS OF PHASE CHANGE AND OF REACTION

When these quantities are measured under conditions of constant volume, they are equal to the change in internal energy of the process in question.
More usually, however, they are measured at constant pressure and are equal to the change in enthalpy (provided that pdV is the only form of work).

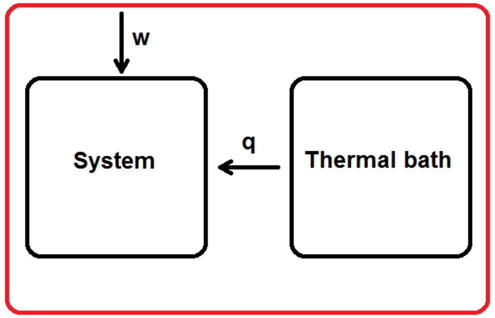
For example, in the vaporization of a pure liquid at constant pressure, the latent heat is:

$$L = H_g - H_l$$

Where g and l denote gas and liquid respectively.

WHAT IS THE PHYSICAL MEANING OF THE FREE ENERGIES?

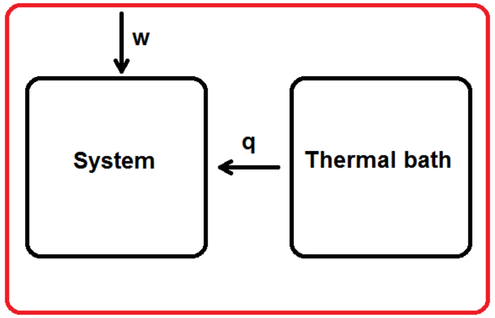
Let’s consider a closed system that undergoes some change from initial state I to a final state F. The system can be in contact with a thermal bath, which is at temperature T_{therm}. Together they are in an adiabatic enclosure.



Closed, adiabatic boundary

WHAT IS THE PHYSICAL MEANING OF THE FREE ENERGIES? CONT'ED

Let's consider a closed system that undergoes some change from initial state I to a final state F. The system can be in contact with a thermal bath, which is at temperature T_{therm}. Together they are in an adiabatic enclosure.



Closed, adiabatic boundary

WHAT IS THE PHYSICAL MEANING OF HELMHOLTZ FREE ENERGY?

$$w_{sys} = [\, A_F^{Sys} - (T_{therm} - T_F^{Sys}) S_F^{Sys}] - [\, A_I^{sys} - (T_{therm} - T_I^{Sys}) S_I^{Sys}] + T_{therm} \Delta S_{glob}$$

During a monothermal process of a system which is at the same temperature as the thermal reservoir in its initial and final state, **the change in *A* of the system corresponds to the minimum amount of work that must be done on the system** to achieve the change.

During a monothermal process of a system which is at the same temperature as the thermal reservoir in its initial and final state, **the change in *A* of the system corresponds to the maximum amount of work that can be obtained from the system**.

WHAT IS THE PHYSICAL MEANING OF GIBBS FREE ENERGY?

$$w_{sys} = [G_F - p_F V_F - (T_{therm} - T_F)S_F] - [G_I - p_I V_I - (T_{therm} - T_I)S_I] + T_{therm}\Delta S_{glob}$$

During a monothermal and monobaric process of a system *receiving work*, **the change in *G* of the system corresponds to the minimum amount of *work other than work due to volume change* that must be done on the system** to achieve the change.

During a monothermal and monobaric process of a system *supplying work*, **the change in *G* of the system corresponds to the maximum amount of *work other than work due to volume change* that can be obtained from the system**.

CRITERIA OF EQUILIBRIUM IN TERMS OF THE EXTENSIVE PROPERTIES

We now envisage a closed system in contact with a thermal reservoir that undergoes an isothermal infinitesimal change during which it cannot exchange work under any form with its surroundings.

A spontaneous evolution of an *isothermal closed* system that *does not exchange work* under any form with its environment takes place in such a way that A decreases. **The system will be at equilibrium when A reaches its minimum value.**

A spontaneous evolution of an *isothermal isobaric closed* system that *exchanges only work due to its volume change* with its environment takes place in such a way that G decreases. **The system will be at equilibrium when G reaches its minimum value**.

THE FUNDAMENTAL EQUATIONS IN TERMS OF U, H, A, AND G & THE NATURAL VARIABLES OF EACH FUNCTION

We will now open the system and consider systems having only one single phase.

THE FUNDAMENTAL EQUATIONS IN TERMS OF U, H, A, AND G & THE NATURAL VARIABLES OF EACH FUNCTION

$$dU = TdS - pdV \qquad dH = TdS + Vdp \qquad dA = -SdT - pdV \qquad dG = -SdT + Vdp$$

If you know the natural variables of a state function, you can define the derivative of this function by its partial derivative expression. Let’s look at the partial derivatives of U, H, A, G with respect to their natural variables.

THE CHEMICAL POTENTIAL

The chemical potential was introduced by J. Willard Gibbs and it is defined as:

$$\mu_i = \left(\frac{\partial \boldsymbol{U}}{\partial n_i}\right)_{\mathbf{S},\,\mathbf{V},\,nj\neq ni} = \left(\frac{\partial \boldsymbol{H}}{\partial n_i}\right)_{\boldsymbol{S},\,\boldsymbol{p},\,nj\neq ni} = \left(\frac{\partial \boldsymbol{A}}{\partial n_i}\right)_{\boldsymbol{T},\,\boldsymbol{V},\,nj\neq ni} = \left(\frac{\partial \boldsymbol{G}}{\partial n_i}\right)_{\boldsymbol{T},\,\mathbf{p},\,nj\neq ni}$$

The chemical potential has an important function, analogous to temperature and pressure. A difference in chemical potential may be regarded as the cause of a chemical reaction or a tendency of a substance to diffuse from one phase into another. The chemical potential is a kind of ”chemical pressure” and it is an intensive property of the system.

SUMMARY: FUNDAMENTAL EQUATIONS OF STATE FOR OPEN SYSTEMS

The basic equations are:

$$dU = TdS - pdV + \sum_i \mu_i \, dn_i$$

$$dH = TdS + Vdp + \sum_i \mu_i \, dn_i$$

$$dA = -SdT - pdV + \sum_i \mu_i \, dn_i$$

$$dG = -SdT + Vdp + \sum_i \mu_i \, dn_i$$

From these, the following equations can be extracted:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} = \left(\frac{\partial H}{\partial S}\right)_{p,n_i}$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,n_i} = -\left(\frac{\partial A}{\partial V}\right)_{T,n_i}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n_i} = -\left(\frac{\partial A}{\partial T}\right)_{V,n_i}$$

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} = \left(\frac{\partial H}{\partial p}\right)_{S,n_i}$$

CHANGE OF CHARACTERISTIC VARIABLES

One can change the characteristic variables of *U*, *H*, *A*, and *G*, according to what fits best the experiment. Below, we will change the characteristic variables of internal energy from $U=U(S, V, n_i)$ to variables that we can measure easier $U=U(T, V, n_i)$. We will do the transformation in a closed system.

$$dU = TdS - pdV$$

MATHEMATICAL RELATIONS BETWEEN THE VARIOUS FUNCTIONS OF STATE: MAXWELL'S RELATIONS

An additional number of useful identities, know as Maxwell's relations, can be obtained by applying a theorem of the calculus concerning exact differentials (Euler's reciprocal relation). Maxwell's relations are relationships between partial derivatives.

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)$$

For example, let consider the internal energy:

SUMMARY: IMPORTANT MAXWELL'S RELATIONS

$$\left(\frac{\partial T}{\partial V}\right)_{S,n_i} = -\left(\frac{\partial p}{\partial S}\right)_{V,n_i}$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,n_i} = \left(\frac{\partial V}{\partial S}\right)_{p,n_i}$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,n_i} = \left(\frac{\partial p}{\partial T}\right)_{V,n_i}$$

$$-\left(\frac{\partial S}{\partial p}\right)_{T,n_i} = \left(\frac{\partial V}{\partial T}\right)_{p,n_i}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n_i,n_j} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i,n_j} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{V,n_i,n_j} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,V,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{S,n_i,n_j} = \left(\frac{\partial V}{\partial n_i}\right)_{S,p,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial S}\right)_{V,n_i,n_j} = \left(\frac{\partial T}{\partial n_i}\right)_{V,S,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{S,n_i,n_j} = -\left(\frac{\partial p}{\partial n_i}\right)_{V,S,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{V,S,n_{k\neq j}} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{V,S,n_{k\neq i}}$$

METHOD FOR CHOICE OF MAXWELL'S RELATIONS

Suppose you want to understand how the entropies of materials change as you squeeze them: $\left(\frac{\partial S}{\partial p}\right)_{T,n_i}$

First, identify what independent variables are needed.

Second, find the natural function of these variables.

Third, express the total deferential of the natural function.

Fourth, based on Euler's reciprocal relation, set equal the two cross derivatives you want.

The Maxwell's relation gives you a quantity you cannot measure $\left(\frac{\partial S}{\partial p}\right)_{T,n_i}$ from a quantity that is easy to measure $\left(\frac{\partial V}{\partial T}\right)_{p,n_i}$