MSE-204 Thermodynamics for Materials Science

L2. AUXILIARY FUNCTIONS & THEIR MEANING

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

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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:

$$dU = \delta q + \delta w$$

And for a reversible, quasi-static change we can substitute: $\delta q = TdS$ $\quad \delta w = -pdV$

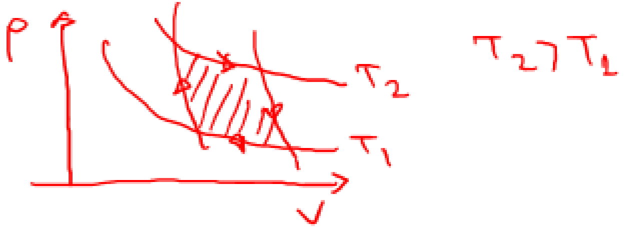
$$\Rightarrow \boxed{dU = T\underline{dS} - p\underline{dV}}$$

$$U = U(\underbrace{S, V}_{\text{natural variables}}) \text{ for a closed system}$$

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: $\oint dU = 0 \Rightarrow \oint TdS = \oint pdV$



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

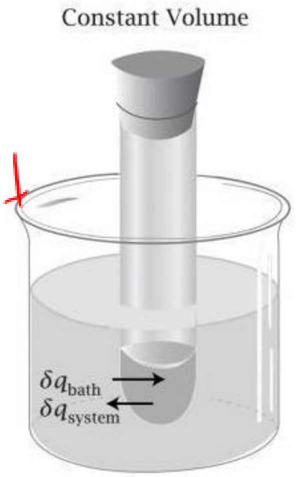
DESCRIPTION OF THERMODYNAMIC SYSTEM

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

S
U
V | extensive variables

T
P | intensive variables

n_i : composition of each component



INTRODUCTION OF AUXILIARY FUNCTIONS

$\equiv \Rightarrow =:$

definition

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

1. $H \equiv U + pV$ enthalpy
2. $A \equiv U - TS$ Helmholtz free energy
3. $G \equiv H - TS$ Gibbs free energy

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

$$f = f(x_1, x_2, x_3, \ldots, x_i, \ldots, x_n)$$

$$g = f - f_i x_i \quad \text{where} \quad f_i = \left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq x_i} \Rightarrow g = g(x_1, x_2, x_3, \ldots, f_i, x_n)$$

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

THE MEANING OF INTERNAL ENERGY DURING ISOCHORIC PROCESSES

First, we will look at an isochoric transformation: ① $dV = 0$

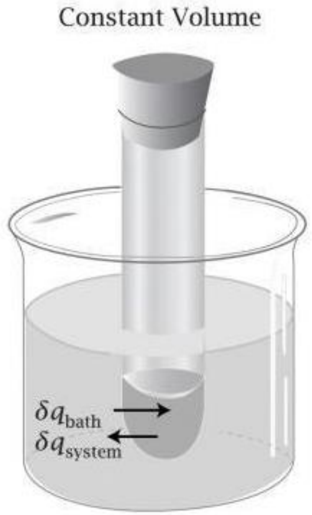
② closed system

③ work only due to volume work

$$dU = \delta q + \delta w = TdS - \cancel{pdV}^{0}$$

$$\Rightarrow \quad dU = TdS = (\delta q)_V$$

internal energy is the ideal function to use when the change of volume is zero.


Constant Volume

THE MEANING OF ENTHALPY DURING ISOBARIC PROCESSES

①

Let’s look at an isobaric transformation: $dp = 0$

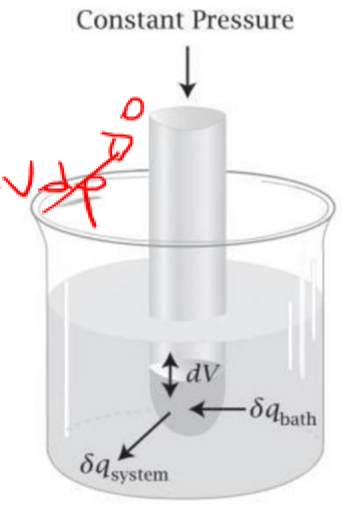
② closed system

③ work only due to volume work

$$dH = d(U + pV) = dU + pdV + Vdp = TdS \cancel{- pdV} \cancel{+ pdV} + V\overset{0}{\cancel{dp}}$$

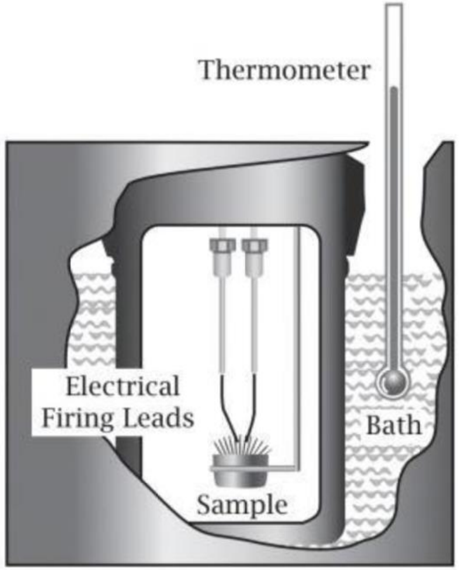
$$dH = TdS = (\delta q)_p$$

the enthalpy is the ideal function to use when the change of pressure is zero.



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:

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

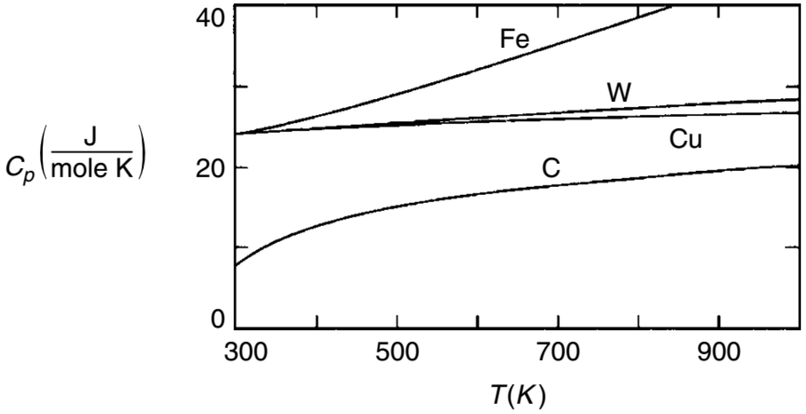
$$dV = 0$$

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

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).

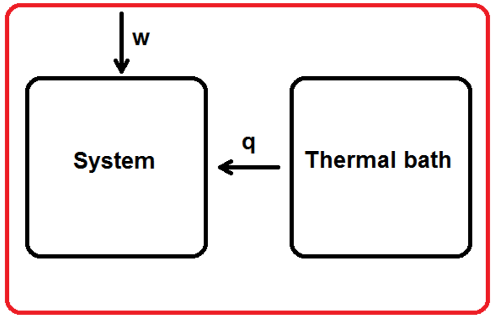
For example, in the vaporization of a pure liquid at constant pressure, the latent heat is:

$$L = H_g - H_l$$

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

$T_{therm} = T$

$q_{therm} = -q_{sys}$

First Law for the system:

$$\Delta U_{sys} = (U_F - U_I)_{sys} = q_{sys} + w_{sys} =$$

$$\Rightarrow \quad q_{sys} = (U_F - U_I)_{sys} - w_{sys} \quad (1)$$

2nd Law for the thermal bath

$$\Delta S_{therm} = \frac{q_{therm}}{T_{therm}} = -\frac{q_{sys}}{T_{therm}} \overset{(1)}{=} -\frac{(U_F - U_I)_{sys} - w_{sys}}{T_{therm}} \quad (2$$

2nd Law Globally

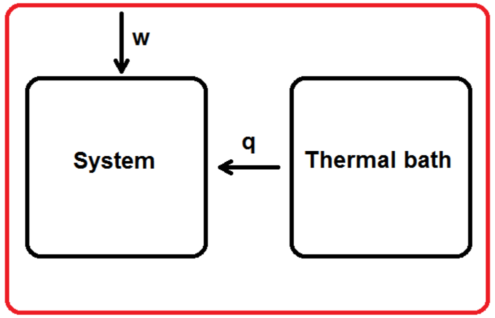
$$\Delta S_{glob} = \Delta S_{therm} + \Delta S_{syst} \overset{(2)}{=} -\frac{\left((U_F - U_I)_{sys} - w_{sys}\right)}{T_{therm}} + \Delta S$$

Solve for w_{sys} $\Rightarrow$

$$\boxed{w_{sys} = (U_F - U_I)_{sys} - T_{therm}(S_F - S_I)_{sys} + T_{therm}\Delta S_{glob}}$$

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.



w

System

q

Thermal bath

Closed, adiabatic boundary

$$w_{sys} = (U_F - U_I)_{sys} - T_{therm}(S_F - S_I)_{sys} + T_{therm}\Delta S_{glob}.$$

Helmholtz free energy:

$$A = U - TS \quad : \quad A_I = U_I - T_I S_I$$

$$A_F = U_F - T_F S_F$$

Gibbs free energy:

$$G = H - TS = U + pV - TS \quad : \quad G_I = U_I + p_I V_I - T_I S_I$$

$$G_F = U_F + p_F V_F - T_F S_F$$

WHAT IS THE PHYSICAL MEANING OF HELMHOLTZ FREE ENERGY?

is associated with the TOTAL work performed by / to the system

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

$T_{therm} = T_F = T_I = T$

$$\boxed{w_{sys} = (A_F - A_I)_{sys} + T_{therm}\Delta S_{glob}}$$

total work → A

$w > 0$ For reversible processes

$$w_{sys} = \Delta A_{sys}.$$

For irreversible process

$$w_{sys} > \Delta A_{sys} \qquad \underbrace{T_{therm}\Delta S_{glob}}_{\text{extra energy}}$$

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.

$w < 0$ For reversible process

$$-w_{sys} = -\Delta A_{sys}$$

For irreversible processes

$$-w_{sys} < -\Delta A_{sys}$$

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?

associated with work that is NOT volume work

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

$T_{therm} = T_I = T_F = T$

$p_{ext} = p_I = p_F$ $\Rightarrow$ $w_{sys} = (G_F - G_I)_{sys} - p_{ext}(V_F - V_I)_{sys} + T_{therm}\Delta S_{glob}$

$w_{volume} = -p_{ext}(V_F - V_I)_{sys}$

$\Rightarrow$ $w_{sys} = w_{volume} + w_{other}$

$$\Rightarrow \boxed{w_{other} = (G_F - G_I)_{sys} + T_{therm}\Delta S_{glob}}$$

$w > 0$ For reversible processes

$w_{sys} = \Delta G$

For irreversible processes

$w_{sys} > \Delta G$ $T_{ther}\Delta S_{glob}$

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.

$w < 0$ For reversible processes

$-w_{sys} = -\Delta G$

For irreversible processes

$-w_{sys} < -\Delta G$ $T_{therm}\Delta S_{glob}$

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.

Helmholtz free energy

$$dA \leq \delta w$$

At equilibrium, workless process

$$dA \leq 0$$

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.**

Gibbs free energy

$$dG \leq \delta w_{other}$$

$$dG \leq 0$$

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.

$$dU = TdS - pdV \;\Big|\; + \ldots \qquad U = U(S, V, n_i)$$

closed system, only volume work

$$dH = d(U + pV) = TdS - \cancel{pdV} + Vdp + \cancel{pdV} \;\Big|\; dH = TdS + Vdp \qquad H = H(S, p, n_i)$$

$$dA = d(U - TS) = \cancel{TdS} - pdV - SdT - \cancel{TdS} \;\Big|\; dA = -SdT - pdV \qquad A = A(T, V, n_i)$$

$$dG = d(H - TS) = \cancel{TdS} + Vdp - \cancel{TdS} - SdT \;\Big|\; dG = -SdT + Vdp \qquad G = G(T, p, n_i)$$

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.

$$U = U(S, V, n_i) \Rightarrow dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,n_i}}_{T\,=} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,n_i}}_{-p\,=} dV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j \neq n_i} dn_i$$

$$H = H(S, p, n_i) \Rightarrow dH = \underbrace{\left(\frac{\partial H}{\partial S}\right)_{p,n_i}}_{T\,=} dS + \underbrace{\left(\frac{\partial H}{\partial p}\right)_{S,n_i}}_{V\,=} dp + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j \neq n_i} dn_i$$

$$A = A(T, V, n_i) \Rightarrow dA = \underbrace{\left(\frac{\partial A}{\partial T}\right)_{V,n_i}}_{-S\,=} dT + \underbrace{\left(\frac{\partial A}{\partial V}\right)_{T,n_i}}_{-p\,=} dV + \sum_i \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j \neq n_i} dn_i$$

$$G = G(T, p, n_i) \Rightarrow dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{p,n_i}}_{-S\,=} dT + \underbrace{\left(\frac{\partial G}{\partial p}\right)_{T,n_i}}_{V\,=} dp + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j \neq n_i} dn_i$$

chemical potential

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.