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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REMINDER FROM LAST WEEK

what is thermodynamics

state functions — process functions

$T, P, U, S, V \quad \oint dF = 0$ — w, q

0th establishes the existence of T

1st " the conservation of energy

2nd " the a quantity called entropy (S) exist, it is a state function, and it value is such that

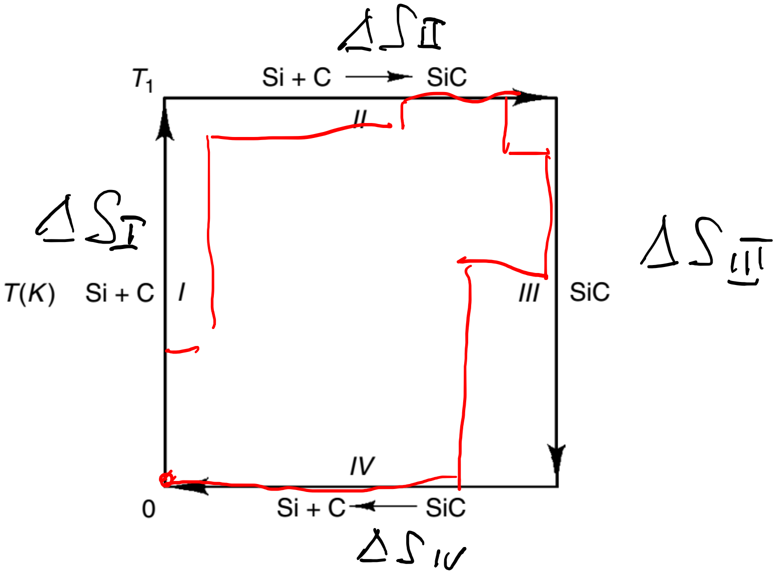
$$dS = \frac{\delta q}{T}$$ in a reversible process

(a) Heat In (b) Work Performed (c) Heat Out

THIRD LAW

Near the turn of the last century, experiments studying the behavior of matter at very low temperatures established that there is a lower limit to the temperature that matter can exhibit.

To illustrate the principle, consider the following cyclic process. A system consisting of one mole of pure silicon and one mole of carbon is initially at temperature zero, and is then heated from 0 to 1500 K.



$$\Delta S = \Delta S_I + \Delta S_{II} + \Delta S_{III} + \Delta S_{IV} = 0$$

$$\Delta S_I + \Delta S_{II} + \Delta S_{III} = 0$$

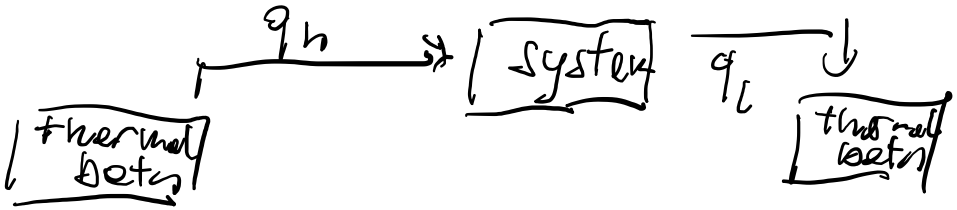
there is alway a T where ∃ $\quad \Delta S_{IV} = 0$

$$T = 0\,K$$

The third law of thermodynamics states:

> There exists a lower limit to the temperature that can be attained by matter, called the absolute zero of temperature and the entropy of all substances is the same at that temperature.

SECOND LAW



$$\frac{q_l^1}{q_h^1} = \frac{q_l^2}{q_h^2} = \frac{T_l}{T_h}$$

Under a given set of conditions, a system can be imagined to undergo several processes in which the energy is conserved (first law). However, it is common experience to observe that the only processes which occur are those which bring the system to a state of rest, i.e. to a state of equilibrium. By considering that this state of equilibrium is a property of the system, thus this state can be described by a function, the second law of thermodynamics determines the direction and extent of such processes. **It affirms the existence of a state function, the entropy S, which for all reversible processes is defined by:**

$$\to dS = \frac{\delta q^{rev}}{T}$$

$$\oint dS = 0$$

$$\boxed{dS = \frac{\delta q}{T}}$$

$$T\,dS = \delta q$$

and for all irreversible processes is such that:

Clausius (ETHZ)

$$= \oint \frac{\delta q}{T} \leq 0$$

$$\to dS > \frac{\delta q^{irr}}{T}$$

$\underbrace{en}_{in}\underbrace{tropy}_{conversion}$

$$\frac{q_l}{T_l} + \frac{q_h}{T_h} = 0$$

Specifically stated, in every volume element of every system and surroundings that may be experience change, the entropy production is positive. HOWEVER, this does not imply that the entropy of a system can only increase.

RELATIONSHIP BETWEEN ENTROPY TRANSFERRED AND HEAT ABSORBED

A quantitative treatment of entropy transfer for reversible processes establishes a connection between the reversible heat flow across the boundary of the system and its change in entropy. The argument applies to any system that is taken through a reversible process.

Let δq_{rev} be the heat absorbed by the system during an infinitesimal step in the reversible process. The system is at temperature T. The differential form $\frac{\delta q_{rev}}{T}$ has units J/K. The sum of the values of this differential form is the sequence of states traversed for the process. The sum has the mathematical form of a line integral along the path:

$$\oint \frac{\delta q}{T}$$

The consequence is that although δq_{rev} is a path-dependent variable ,$\frac{\delta q_{rev}}{T}$ is the differential of a state function.

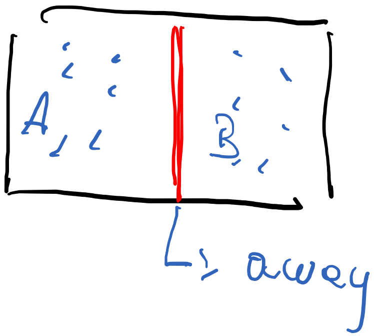
The state function is then defined to be the entropy of the system:

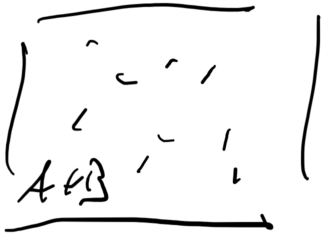
$$\delta q_{rev} = T dS_{syst} \text{ and } q_{rev} = \oint T dS_{syst}$$

which permits the computation of the heat absorbed for any reversible process by integration of the combinations of the state functions of temperature and entropy

ENTROPY CONDITION FOR EQUILIBRIUM

In the equilibrium state of a process, the entropy is a maximum. Any variation about the equilibrium state can only decrease the entropy.



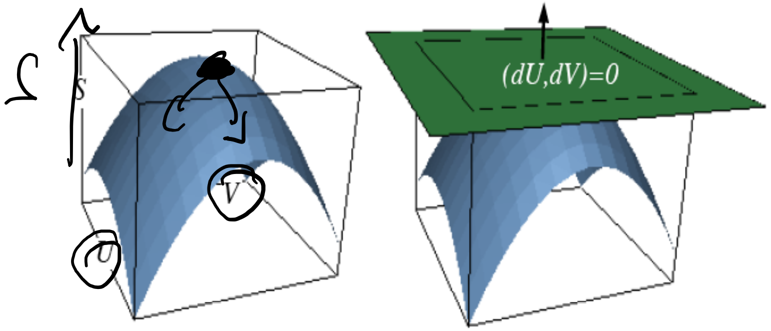


adiabatic (also isolated) way

$\delta S \leq 0$

$\boxed{dS \leq 0}$

@ equilibrium



In general for systems of constant internal energy and volume, the condition of equilibrium is the attainment of the maximum entropy.

EQUIVALENT STATEMENTS OF THE SECOND LAW

Clausius:

Heat never spontaneously flows from an object of lower temperature to one of higher temperature

Kelvin:

It is impossible to continuously perform work by cooling a body to a temperature below that of the lowest temperature of its surrounding

Kelvin:

Using a system which undergoes a cyclic thermodynamic process, it is impossible to obtain usable work if globally heat is only exchanged with one thermal reservoir

Ostwald:

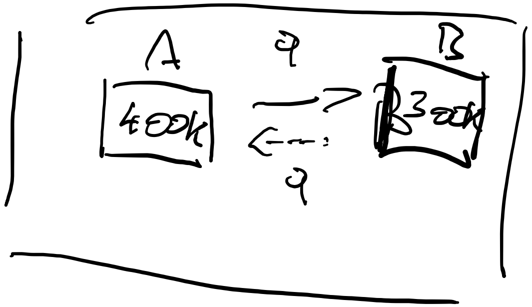
A perpetual motion machine “of the second type” has never been observed

Caretheodory:

In the neighborhood of every thermodynamic state that can be reached by a reversible path, there exists states which cannot be reached along a reversible adiabatic path (isentropic), or which can be reached either irreversibly or not at all

ENTROPY | Example: Hot bodies in contact

Consider the passage of heat from a hot body to a cold one, with no other work being performed. Consider two very large bodies, one at T=400K and the other at T=300K.



Case 1: Suppose 400 Joules of heat are transferred from hot object A to the cooler body B

$q_B = 400 J$ $q_A = -400 J$

$\Delta S_B = \frac{400 J}{300 K} = \frac{4}{3} J/K$ $\Delta S_A = -1 J/K$

$\Delta S_{sys} = \Delta S_A + \Delta S_B = \frac{1}{3} J/K$

Case 2: Suppose 400 Joules of heat are transferred from cold object B to the hotter body A

$q_B = -400 J$ $q_A = 400 J$

$\Delta S = -\frac{4}{3} J/K$ $\Delta S_A = 1 J/K$

$\Delta S_{sys} = -\frac{1}{3} J/K$

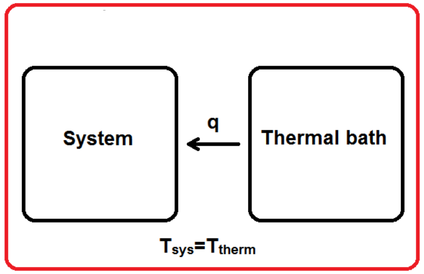
ENTROPY IMPLICATIONS: SPONTANEITY

We now consider a closed adiabatic system. We assume this system evolves spontaneously and adiabatically from initial state I to final state F. Let us know imagine a reversible, isothermal process that brings the system back from state F to state I. During this part of the process, the system can eventually exchange heat with a thermal reservoir. The first law for the total process states:

do this @ home

HEAT ABSORBED IN REVERSIBLE VS IRREVERSIBLE PROCESSES

We investigate next an infinitesimal process of a closed system. This system can exchange heat with only one thermal reservoir at temperature T_{therm}. The global system is a closed adiabatic system. The system receives an amount of heat and since the global system is adiabatic, the amount of heat received by the thermal reservoir is:



Closed, adiabatic boundary

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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:

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

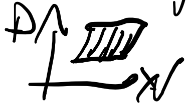
And for a reversible, quasi-static change we can substitute: $\delta q = TdS$ $\quad \delta w = -pdV$

$$dU = TdS - pdV \qquad U(S, V)$$

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: $\oint dU = 0 = \oint TdS - \oint pdV \qquad \oint TdS = \oint pdV$



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?

U
S
V
| extensive

T
P
| intensive

n_i ← Composition

$$U(S, V, n_i)$$

$$dU = T\,dS - p\,dV + \sum_i \frac{\partial U}{\partial n_i}\,dn_i$$

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. $H = U + pV$ enthalpy
2. $A = U - TS$ Helmoltz free energy
3. $G = H - TS = U + pV - TS$ Gibbs free energy

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

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

(1)

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

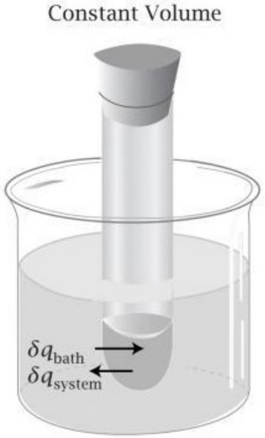
(2) closed system

(3) work is only due to change in volume

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

$$dU = TdS$$

$$dU = (\delta q)_V$$



THE MEANING OF ENTHALPY DURING ISOBARIC PROCESSES

(1)

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

$$U(S,V) \longrightarrow H(S,p)$$

(2) & (3) the same

$$H = U + pV$$

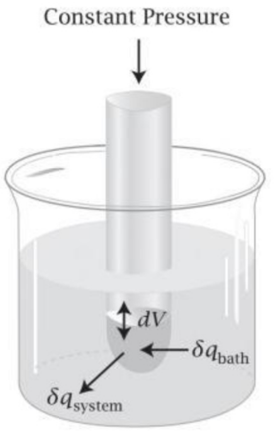
$$dH = dU + d(pV) = TdS - p\cancel{dV} + p\cancel{dV} + Vdp =$$

$$= TdS + V\cancel{dp}$$

$H(S,p)$

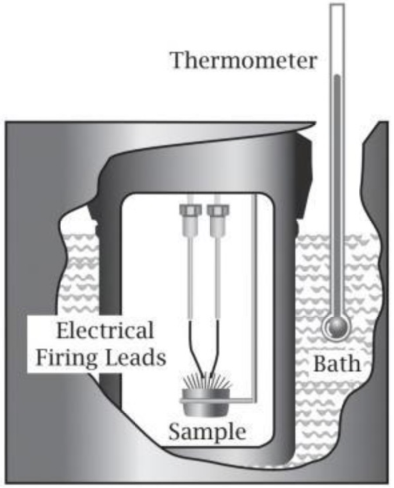
$$dH = TdS$$

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



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:

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

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:

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

$$dV = 0$$

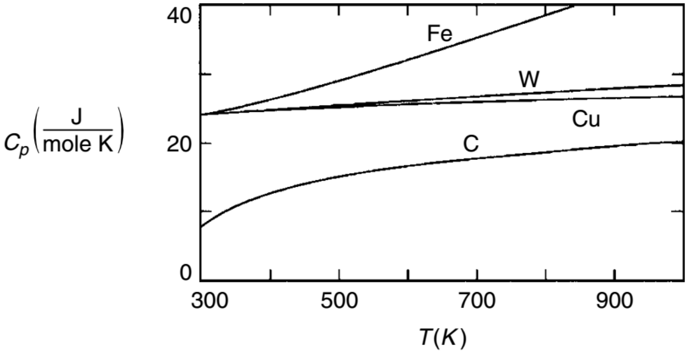
$$C_V = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$

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

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

extensive

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).

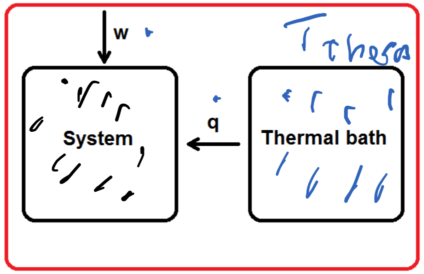
For example, in the vaporization of a pure liquid at constant pressure, the latent heat is:

$$\boxed{L = H_g - H_l}$$

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

1st law for the system

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

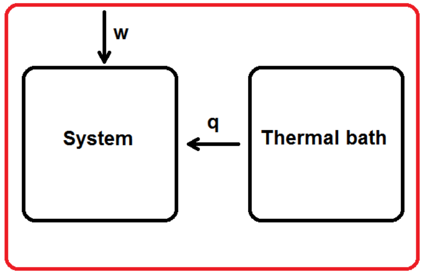
2 law of thermo

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

$$\Delta S_{glob} = \Delta S_{therm} + \Delta S_{syst} = -\frac{(U_F - U_I) - w_{sys}}{T_{therm}} + \Delta S_{syst}$$

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

$$W_{sys,t} = (U_F - U_I)_{sys} - T(S_F - S_I)_{sys} + T\Delta S_{glob}$$

$$A = U - TS$$

$$\boxed{\begin{aligned} A_I &= U_I - T_I S_I \\ A_F &= U_F - T_F S_F \end{aligned}}$$

$$G = U + PV - TS \Rightarrow G_i = U_i + P_i V_i - T_i S_i$$

WHAT IS THE PHYSICAL MEANING OF HELMHOLTZ FREE ENERGY?

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

if $T_{therm} = T_I^{sys} = T_F^{sys}$

$$w = \Delta A^{sys} + T\,\Delta S^{glob}$$

if reversible process

then $\Delta S^{glob} = 0$

$\hookrightarrow \quad w^{sys} = \Delta A$

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?

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

$$T_{therm} = T_I^{sys} = T_P^{sys} = T$$

$$w = \Delta G - \Delta(pV) + T\Delta S$$

if the process is reversible

$$w = \Delta G - \Delta(pV)$$

$$w = w^v + w^o$$

$$w^v = -\Delta(pV)$$

$$w^o = \Delta G$$

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.

dA min

$dA \leq 0$

constant V

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.**

dG min

$dG \leq 0$

constant p

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.

$$dU = TdS - pdV \qquad U(S, V, n_i)$$

$$dH = TdS + Vdp \qquad H(S, p, n_i)$$

$$dA = dU - d(TS) = \cancel{TdS} - pdV - \cancel{TdS} - SdT = -pdV - SdT$$

$$A(V, T, n_i)$$

$$dG = dH - d(TS) = \cancel{TdS} + Vdp - \cancel{TdS} - SdT = Vdp - SdT$$

$$G(p, T, n_i)$$

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.

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

$$dH = \left(\frac{\partial H}{\partial S}\right)_{p,n_i} dS + \underset{V}{\overset{T}{\left(\frac{\partial H}{\partial p}\right)_{S,n_i}}} dp + \overset{-p}{\sum_i} \boxed{\left(\frac{\partial H}{\partial n_i}\right)_{p,S} dn_i}$$

$$dA = \overset{T}{\left(\frac{\partial A}{\partial T}\right)_{V,n_i}} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n_i} dV + \sum_i \boxed{\left(\frac{\partial A}{\partial n_i}\right)_{V,T} dn_i}$$

$$dG = \underset{-S}{\overset{-S}{\left(\frac{\partial G}{\partial T}\right)_{p,n_i}}} dT + \underset{V}{\overset{-p}{\left(\frac{\partial G}{\partial p}\right)_{T,n_i}}} dp + \sum_i \boxed{\left(\frac{\partial G}{\partial n_i}\right)_{p,T} dn_i}$$

THE CHEMICAL POTENTIAL

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

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:

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

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

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

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

GIBBS-HELMHOLTZ EQUATIONS

By combining the previous identities with defining equations for A and G, further expressions can be obtained. Specifically, we will look into how the free energy of a system depends on temperature.

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

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

EXAMPLE: INTERNAL ENERGY (& ENTHALPY) OF IDEAL GAS

Earlier, we expressed the internal energy of a closed system using V and T as the characteristic variables:

$$dU = \left\{-p + T\left(\frac{\partial S}{\partial V}\right)_T\right\} dV + T\left(\frac{\partial S}{\partial T}\right)_V dT$$

Through Maxwell's relations we know that:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Therefore, for an ideal gas the variation of internal energy with respect to volume is: