BREF COURS SUR LA THERMODINAMIQUE CLASSIQUE

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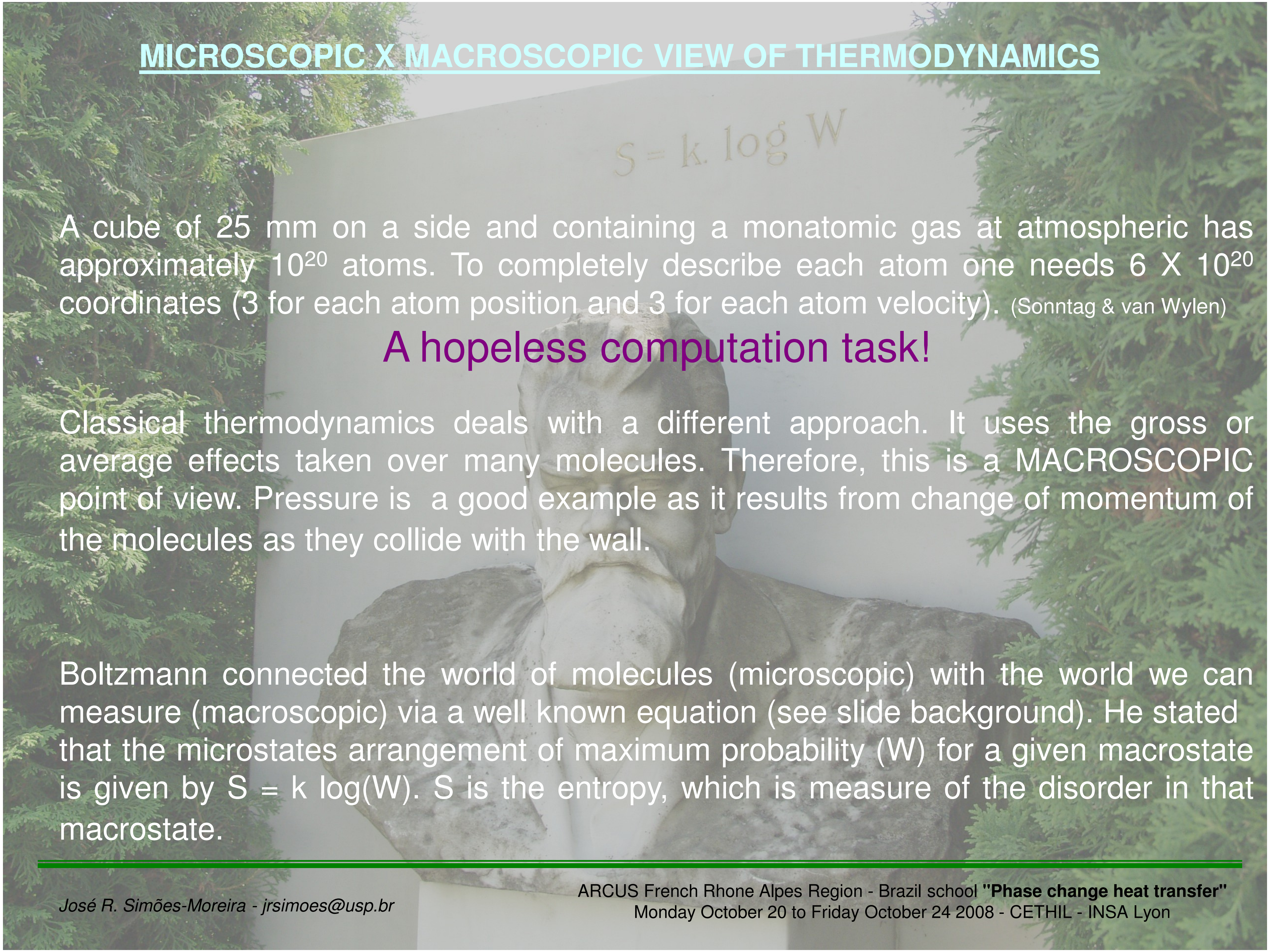


MICROSCOPIC X MACROSCOPIC VIEW OF THERMODYNAMICS

A cube of 25 mm on a side and containing a monatomic gas at atmospheric has approximately 10^{20} atoms. To completely describe each atom one needs 6 X 10^{20} coordinates (3 for each atom position and 3 for each atom velocity). (Sonntag & van Wylen)

A hopeless computation task!

Classical thermodynamics deals with a different approach. It uses the gross or average effects taken over many molecules. Therefore, this is a MACROSCOPIC point of view. Pressure is a good example as it results from change of momentum of the molecules as they collide with the wall.

Boltzmann connected the world of molecules (microscopic) with the world we can measure (macroscopic) via a well known equation (see slide background). He stated that the microstates arrangement of maximum probability (W) for a given macrostate is given by $S = k \log(W)$. S is the entropy, which is measure of the disorder in that macrostate.

THERMODYNAMICS - A THEORY BASED ON EXPERIMENTAL EVIDENCE

In 1865 Clausius (also quoted in *The Scientific Papers of J. Willard Gibbs,* V. 1, Dover, NY, 1961) stated the two basic laws of Thermodynamics:

✓*Die Energy der Welt ist konstant.* (The Energy of the Universe is Constant)

✓*Die Entropy der Welt strebt einem Maximum zu.* (The Entropy of the Universe tends toward a Maximum)

Classical Thermodynamic is build up on those two simple laws.

So far, no one has been able to contradict those statements or laws. All the processes and machines humankind is familiar with do obey such laws.

Therefore,

Thermodynamic is a science based and established on *experimental evidence*.

THERMODYNAMIC TIME TABLE

1798	Count Rumford – heat and work equivalence – canon boring
1799	Sir Humphry Davy – conversion of work into heat, ice-rubbing experiments
1824	Sadi Carnot – reversible cyclic engine - “Reflection on the Motive Power of Fire”
1842	Mayer – principle of conservation of energy
1847	Helmholtz – principle of conservation of energy (independent of Meyer)
1843-1848	James Prescott Joule – first law of thermodynamics
1848	Lord Kelvin (William Thomsom) – absolute temperature
1850	Rudolf J. Clausius – first and second law of thermodynamics
1865	Clausius – defined that the energy of the universe is constant and the entropy of the universe tends toward a maximum
1875	Joisiah Willard Gibbs – thermodynamics in a general form heterogeneous systems and chemical reactions – chemical potential
1897	Max Planck – “It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than the raising of a weight and the cooling of a heat reservoir”
1909	Caratheodory – thermodynamics entirely mathematical in form

SOME DEFINITION OF THERMODYNAMICS

It is supposed that fundamental properties are already known.

That means: pressure (P), temperature (T), volume (V), internal energy (U), entropy (S) are known *a priori*.

Thermodynamic System

A region of the space which is the subject of study. The *system* is separated from the *surroundings*, i. e., everything else outside the system. Both the system and the surroundings make up the *universe*.

Open System – mass can flow in or out, but energy can.

Closed Sytem – mass cannot flow in or out, but energy can.

Isolated System – neither mass nor energy can flow in or out.

HEAT

Heat is the form of energy in transit across the boundary separating a system from its surroundings. A system *does not* contain or store heat. Heat transfer takes place to or from the system due to difference of temperatures between the system and the surroundings. Heat *is not* associate with mass transfer. Heat added to a system is a positive number, whereas heat transfered from a system is a negative number. The SI unit of heat is joule, J.

WORK

Mechanical work is given by a force *F* acting on a system moves through a distance *x*.

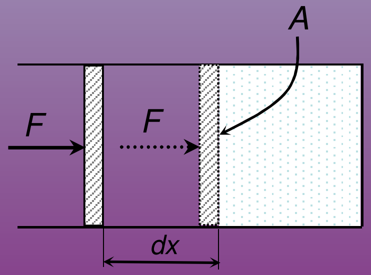
$$W = \int F dx$$

$$W = \int F dx = \int PA dx = \int P dV$$

In differential form: $\boxed{\delta W = P dV}$

The SI unit of work is joule, J.

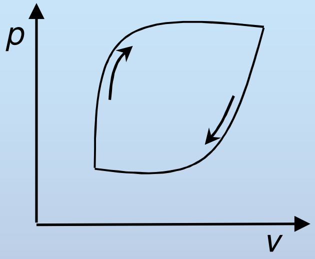
This is the definition of *reversible work.*



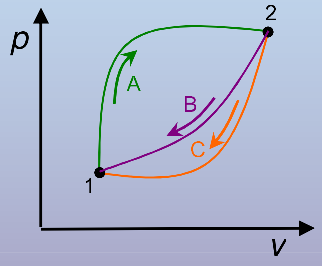
FIRST LAW OF THERMODYNAMICS OR LAW OF CONSERVATION OF ENERGY

Cyclic process:

$$\boxed{\oint \delta Q = \oint \delta W}$$



By opening the cycle into two processes, one obtains:



processes A and B

$$\oint \delta Q = \int_1^2 \delta Q_A + \int_2^1 \delta Q_B = \int_1^2 \delta W_A + \int_2^1 \delta W_B = \oint \delta W$$

processes A and C

$$\oint \delta Q = \int_1^2 \delta Q_A + \int_2^1 \delta Q_C = \int_1^2 \delta W_A + \int_2^1 \delta W_C = \oint \delta W$$

Subtracting both equations

$$\boxed{\int_1^2 (\delta Q - \delta W)_B = \int_1^2 (\delta Q - \delta W)_C = \int_1^2 \underbrace{(\delta Q - \delta W)}_{\text{any process between 1 and 2}} = \int_1^2 dE}$$

Heat and work are not state function, but their difference is. The amount ($\delta Q - \delta W$) depends just on the initial and final thermodynamic states 1 and 2.

First law for a process differential form

$$\boxed{dE = \delta Q - \delta W}$$

E is the total energy (joules) of the system, which may be: Kinetic, gravitational potential, chemical, internal, others

First law for a process integral form

$$\boxed{\int_1^2 dE = \int_1^2 \delta Q - \int_1^2 \delta W \Rightarrow E_2 - E_1 = {}_1Q_2 - {}_1W_2}$$

Notation
W>0 – system produces net work
Q>0 – heat is added to the system

FIRST LAW OF THERMODYNAMICS (*cont...*)

If the only form of energy relevant is the internal energy *(U), then:*

Integral form $\boxed{U_2 - U_1 = {}_1Q_2 - {}_1W_2}$ *differential form* $\boxed{dU = \delta Q - \delta W}$

Generally in thermodynamic analyses are allowed to neglected other forms of energy, except when one is dealing with reacting systems (*combustion and other chemical reactions*), high speed flow (*kinetic energy is important*), magnethydrodynamics (*electric field*), to name a few other form of energies.

On the other hand, other forms of energy may play the most important role in other systems. Such is the case of hydropower electrical generation, where gravitational potential energy of water stored in dams is transformed into mechanical work (turbomachines).

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SECOND LAW OF THERMODYNAMICS

Entropy S – there is a thermodynamic property called entropy defined according to:

$$\boxed{dS = \left(\frac{\delta Q}{T}\right)_{rev}}$$

The index “*rev*” means a reversible heat exchange

“The total entropy variation of any system and its surroundings is positive and it approaches zero for reversible process”. It is also known as “the principle of increase of the entropy of the Universe”

$$\boxed{\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \geq 0}$$

Example: Supposing that human beings loose 100 W of heat flux to the environment to keep its internal temperature (36 °C). For sake of a quick estimation, suppose that this heat flux is basically lost by convection (which is not true, because of the respiration process). Calculate the amount of total entropy generated in one hour if the environment is at 25 °C.

$$\Delta S_{total} = \Delta S_{human} + \Delta S_{environ} = \left(-\frac{100}{36 + 273.15} + \frac{100}{25 + 273.15}\right) \times 3600 = 42{,}96 \ {}^{J}\!/_{K}$$

FUNDAMENTAL PROPERTY RELATION FOR A PVT SYSTEM

Considering that $TdS = \delta Q$ and $PdV = \delta W$ for reversible processes, then by substitution in the first law equation, one obtains the fundamental property relation

$$\boxed{dU = TdS - PdV}$$

Even though this relation was developed for particular processes (reversible) it involves thermodynamic properties only and, therefore, is always valid, nevertheless of the process. This relation is also known is The Gibbs Equation.

In this thermodynamic property relation, the internal energy U is function of S and V, i.e., $U = U(S,V)$. Considering that the fundamental property relation is *exact*, then, it is possible to write down:

$$dU = \left.\frac{\partial U}{\partial S}\right)_V dS + \left.\frac{\partial U}{\partial V}\right)_S dV$$

By comparing both equations, one obtains:

$$T = \left.\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad P = -\left.\frac{\partial U}{\partial V}\right)_S$$

where, T is said to be the *conjugate variable* of S and P is the *conjugate variable* of V.

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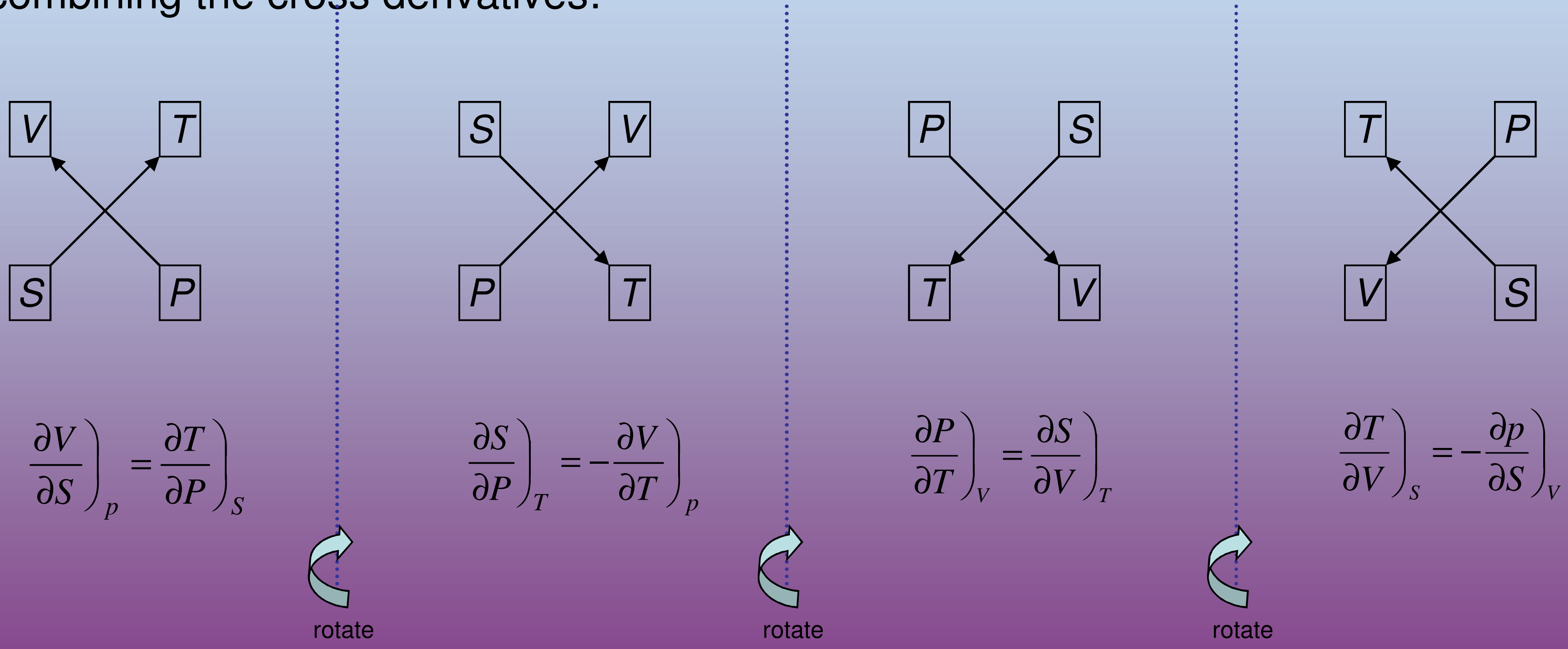
Maxwell Relations

As mentioned, the fundamental property relation $U = U(S,V)$ is EXACT from the mathematical point-of-view. Thus, one may obtain the well known Maxwell relations. A rotating diagram is usually used as a rule-of-thumb to recall the 4 possibilities of combining the cross derivatives:



$$\left.\frac{\partial V}{\partial S}\right)_p = \left.\frac{\partial T}{\partial P}\right)_S$$

$$\left.\frac{\partial S}{\partial P}\right)_T = -\left.\frac{\partial V}{\partial T}\right)_p$$

$$\left.\frac{\partial P}{\partial T}\right)_V = \left.\frac{\partial S}{\partial V}\right)_T$$

$$\left.\frac{\partial T}{\partial V}\right)_S = -\left.\frac{\partial p}{\partial S}\right)_V$$

Note: symmetrical arrows are for positive values

Legendre Transformations and Thermodynamic Potentials

In the fundamental property relation $dU = TdS - PdV$, the entropy S and volume V are said to be *natural* or *canonical* variables of the internal energy U in any closed system.

However, in many thermodynamic system, it may be useful to have independent variables other than the pair S and V. In engineering, for instance, it is more useful to have pairs of independent variables from the combination of P, T, and V because they are measurable quantities. Similarly, in certain thermodynamic analysis it may be useful to have any other pair of independent variables.

Legendre transformation provides a standard mathematical method for “replacing” the original natural variable pairs by other variables, keeping the consistence with the fundamental property relation.

Legendre Transformations and Thermodynamic Potentials (*cont*...)

By applying the Legendre transformation successively, one obtains:

Action over fundamental relation:	**No action**	**replacing *V* by its conjugate *P***	**replacing *S* by its conjugate *T***	**replacing both *S* and *V***
Potential	***U(S,V)***	***H (P,S)= U + PV***	***A (T,V)= U-TS***	***G(T,P)= U+PV-TS***
Differential form:	***dU = TdS-PdV***	***dH = TdS+VdP***	***dA = -SdT-PdV***	***dG = -SdT+VdP***
Natural variables:	***S* and *V***	***S* and *P***	***T* and *V***	***T* and *P***
Conjugate variables:	***T* and *P***	***T* and *V***	***S* and *P***	***S* and *V***
Mathematical inference:	$T = \left.\frac{\partial U}{\partial S}\right)_V$ and $P = -\left.\frac{\partial U}{\partial V}\right)_S$	$T = \left.\frac{\partial H}{\partial S}\right)_p$ and $V = \left.\frac{\partial H}{\partial P}\right)_S$	$S = -\left.\frac{\partial A}{\partial T}\right)_V$ and $P = -\left.\frac{\partial A}{\partial V}\right)_T$	$S = -\left.\frac{\partial G}{\partial T}\right)_p$ and $V = -\left.\frac{\partial G}{\partial P}\right)_T$
Potential name:	**Internal energy**	**Enthalpy**	**Helmholtz free enrgy**	**Gibbs energy Or Free enthalpy**

Additional Comments over the Fundamental Relation and the Potentials

It is known that for a *P-V-T* system formed by a single compressible substance, the thermodynamic state is determined by any two independent properties (variables). Therefore, one may name by convenience two out of its set of properties to be independent. Any further relation combining these two variables will furnish the thermodynamic state.

P-V-T equations of state are sometimes called *thermal equations of state*. A quite good number of such equations exist, being the ideal gas equation of state, $PV=RT$, one of the simplest relating all of those three variables. However, thermal equations of state *do not* contain all thermodynamic information necessary to describe the system as whole. It is necessary to be given other properties, such the heat capacity.

On the other hand, the fundamental relation *does* encompass all thermodynamic information. All other property relations are derived from it. Likewise, as mentioned, the Legendre transformation scheme does keep the original fundamental relation and, thus, the 3 (three) new thermodynamic potentials do encompass all thermodynamic information as well.

Example of a Equation of State

Consider the following equation of state, where *A* and *B* are positive constants. The index “0” refers to a reference state. Obtain expressions for temperature *T* and pressure *P*.

$$\frac{U}{U_0} = \left(\frac{V}{V_0}\right)^{-A} \times \exp\left(\frac{S - S_0}{B}\right)$$

$$T = \left.\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S}\left[U_0\left(\frac{V}{V_0}\right)^{-A} \times \exp\left(\frac{S - S_0}{B}\right)\right]_V = \frac{U_0}{B}\left(\frac{V}{V_0}\right)^{-A} \times \exp\left(\frac{S - S_0}{B}\right) = \frac{U}{B}$$

$$P = -\left.\frac{\partial U}{\partial V}\right)_S = -\frac{\partial}{\partial V}\left[U_0\left(\frac{V}{V_0}\right)^{-A} \times \exp\left(\frac{S - S_0}{B}\right)\right]_S = \frac{AU_0}{V_0}\left(\frac{V}{V_0}\right)^{-A-1} \times \exp\left(\frac{S - S_0}{B}\right) = \frac{AU}{V}$$

Substituting *U*, one obtains: $PV = RT \quad \text{where } R = AB$

The ideal *P*-*V*-*T* information is “built in” in the given equation of state

Specific Heats and Properties Calculation

Specific Heat at Constant Volume:

$$\boxed{C_V \equiv \left.\frac{\partial U}{\partial T}\right)_V}$$

Specific Heat at Constant Pressure:

$$\boxed{C_P \equiv \left.\frac{\partial H}{\partial T}\right)_P}$$

Now it will be given a set of equations to evaluate thermodynamic properties from measured *P-V-T* data set in conjunction with the heat capacities. It is now convenient to have *U* as function of *T* and *V*, i. e., *U*(*T*,*V*). Thus, from the exactness of *U*:

$$dU = \underset{C_V}{\boxed{\left(\frac{\partial U}{\partial T}\right)_V}} dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

From the fundamental relation $dU = TdS - PdV$

Dividing the equation through by *dV* and restricting it to constant *T*, it gives $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

Using one of the Maxwell relations: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \Rightarrow \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

Finally: $$\boxed{dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV}$$

The internal energy change can be evaluate from *P-V-T* data plus C_V!

Specific Heats and Properties Calculation (*cont...*)

A similar equation can be obtained for *H* change, which is:

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP$$

The enthalpy change can be evaluate from *P-V-T* data plus C_P!

In analogous way, it is possible to obtain

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \quad \text{and} \quad dS = \frac{C_P}{T} dT + \left(\frac{\partial V}{\partial T}\right)_P dP$$

By equating both equations (same *dS* change)

$$\left(C_P - C_V\right) dT = T\left(\frac{\partial V}{\partial T}\right)_P dP + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

Dividing the above equation by *dT* and restricting it to constant volume, it comes

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

A final important relation is the ratio between heat capacities

$$\gamma = \frac{C_P}{C_V} = \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial p}{\partial V}\right)_S$$

Example with the Ideal P-V-T Equation of State

Ideal gas: $PV = RT$

$$\text{useful derivative calculation}: \begin{cases} \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} = \frac{T}{P} \\ \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} = \frac{V}{T} \\ \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT^2}{P^2} = -\frac{V}{P} \end{cases}$$

By substituting the derivatives into the previous relations, one obtains:

Internal energy: $dU = C_V dT \Rightarrow \Delta U = \int_{T_1}^{T_2} C_V dT = \overline{C_V}\,\Delta T$

Enthalpy: $dH = C_P dT \Rightarrow \Delta H = \int_{T_1}^{T_2} C_P dT = \overline{C_P}\,\Delta T$

Entropy (eq. 1): $dS = C_V \frac{dT}{T} + R\frac{dV}{V} \Rightarrow \Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right)$ for C_V constant

Entropy (eq. 2): $dS = C_P \frac{dT}{T} - R\frac{dP}{P} \Rightarrow \Delta S = C_P \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)$ for C_P constant

Heat capacities difference: $C_P - C_V = R$

Heat capacities ratio: $\gamma = \frac{C_P}{C_V} = -\frac{V}{P}\left(\frac{\partial P}{\partial V}\right)_S$

Isentropic process (S=const): $\frac{dP}{P} = \gamma\frac{dV}{V} \Rightarrow PV^{\gamma} = const$

Phase Equilibria Condition for a P-V-T Pure Substance

From the Clausis inequality: $dS_{total} \geq 0 \Rightarrow dS_{system} + dS_{surroundings} \geq 0$

For a reversible heat exchange from the system to the surroundings (both at *T*): $dS_{surroundings} = -\dfrac{\delta Q}{T}$

Thus, $dS_{system} \geq \dfrac{\delta Q}{T}$

On the other hand, from the first law: $\delta Q = dU - PdV$

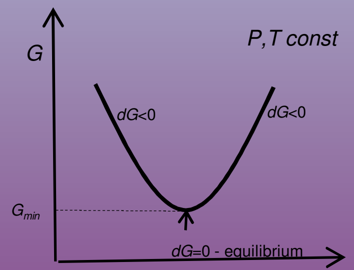
By substitution, it comes to: $\boxed{dU - TdS + PdV \leq 0}$ where the index “system” has been dropped for sake of simplicity. All properties are for the closed system.

Recalling that $G = U + PV - TS \Rightarrow dG = dU + d(PV) - d(TS)$

After some manipulation: $dU - TdS + PdV = dG - VdP + SdT$

Substituting it into the inequality: $\boxed{dG - VdP + SdT \leq 0}$

For a process restricted to *T* and *P* constant, one obtains: $(dG)_{P,T} \leq 0$



The equilibrium will occur when the Gibbs energy is a minimum, i. e., $\boxed{(dG)_{P,T} = 0}$

Phase Equilibria for a Pure Substance

A phase change occurs at constant *P* and *T*, resulting in discontinuous change in most thermodynamic properties, but the Gibbs energy. In liquid-vapor equilibrium system, saturated liquid properties are quite different from the corresponding saturated vapor ones. However, the Gibbs energy must be the same across the phase boundary, as seem above (recall that during phase change *P* and *T* are constant).

Let α be one phase and β the other phase in a α-β phase equilibrium system, thus:

$$(dG)_{P,T} = 0 \Rightarrow dG^{\alpha} = dG^{\beta}$$

Substituting the differential form of Gibbs energy:

$$-S^{\alpha} dT + V^{\alpha} dP = -S^{\beta} dT + V^{\beta} dP \quad \text{or} \quad \frac{dP}{dT} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}}$$

Introducing the saturation index, since *P* is always the saturation one in this equation:

$$\boxed{\frac{dP^{sat}}{dT} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}}$$

The entropy in differential form can be written as: $TdS = dH - VdP$

During a phase change process *P* and *T* are const: $TdS = dH \Rightarrow dS = \frac{dH}{T} \Rightarrow \Delta S^{\alpha\beta} = \frac{\Delta H^{\alpha\beta}}{T}$

Finally, one obtains the Clapeyron Equation:

$$\boxed{\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T \Delta V^{\alpha\beta}}}$$

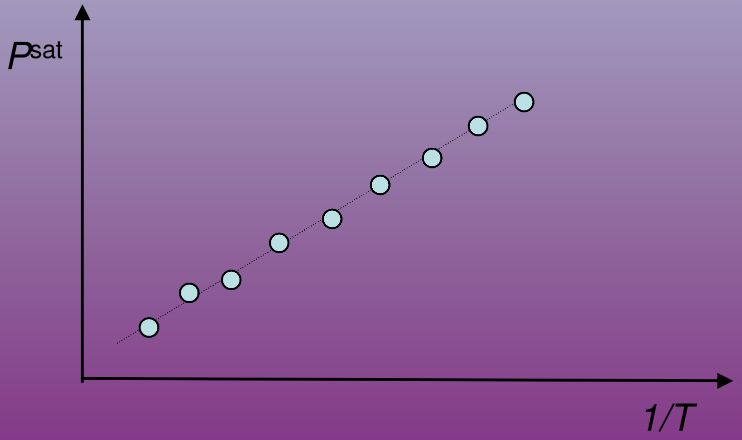
Phase Equilibria for a Pure Substance (*cont...*)

Clapeyron equation relates the slope of the saturation curve with the enthalpy change and the volume change across the two phases.
For a pure substance, phases can be (1) solid-liquid; (2) solid-vapor; and (3) liquid-vapor

From the exact Clapeyron equations, one can obtain practical equations for data fitting. Such is the case of the well known *Antoine equation* that can be used to adjust vapor pressure data using three constants, A. B, and C.

$$\boxed{\ln P^{sat} = A - \frac{B}{T + C}}$$

Usually a plot P^{sat} versus $1/T$ is construct given a nearly straight line.



FINAL REMARKS AND THANKS

Evidently, classic thermodynamics goes much beyond of the material presented here. We did not deal with open system analysis, thermal machine analysis, and other fields of applications of the subject. Here it was presented just the highlights of thermodynamics.

Thanks the ARCUS organization and profs. Julio C. Passos and B. Stutz for the invitation.