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Lecture Notes - General Thermodynamics

Prof. Yarger's Hand Written Lecture Notes

These set of notes started as student lecture notes from a class by Prof. George Wolf. They were further developed over several years of teaching Thermodynamics at the University of Wyoming and Arizona State University. This is a subset of lecture notes on the fundamentals of thermochemistry. The notes have been compiled as a foundation for teaching 'thermodynamics with a biological focus'

ASU BCH 341 - 'Physical Chemistry With A Biological Focus' - i.e. BioPhysical Chemistry
BioPchem: Thermo

Lecture Notes - Set 1 - Topics:

Thermodynamic Concepts (1-11), Mathematics of Thermodynamics (11-16), Reversible Processes (17-18), Adiabatic Accessibility (19), Isochoric Process (20-21), Isobaric Processes (22-24), Sensible Heat (25), Isochoric Calorimeter - Bomb Calorimeter (26-27), Isobaric Calorimetry (28-32), Introduction to Thermochemistry (33-35), Standard States (36), Hess' Law (37), Combustion Rxns (38), Formation Rxns (39), Solution Enthalpy (40-41), Temperature Dependence of Enthalpy (42-43).

Thermodynamic Concepts

System: That part of the universe that is separated out (either physically or mentally) for study.

Surroundings: Everything outside the system.

Walls: (constraints) Restricts the redistribution of some quantity (i.e. mass, heat, ...) either between the system & surroundings or within the system itself.

External Walls: restriction between the system & surrounding.

Internal Walls: (or constraints) restriction within the system (see Callen)

Thermodynamic systems are classified by their walls:

Thermo Qty	Restricted	Not-Restricted
Heat	adiabatic ($\Delta Q = 0$)	Diathermal
Matter	closed ($\Delta N_{ext} = 0$)	open
Chemical Component	Semipermeable ($\Delta N_{i,ext} = 0$)	open
Volume	isochoric ($\Delta V = 0$)	isobaric ($\Delta P = 0$)

→ It is through the manipulation of walls that constraints (either external or internal) are changed and processes initiated.
It is the subject of Thermodynamics which describes these changes & places constraints on what can't happen or what may happen (but not necessarily will happen) in the system. Much of the development of Thermodynamics occurred in the industrial revolution where machines were deviced to extract the most work from chemical and/or mechanical processes.
The Theory of Thermodynamics also provides important relations between macroscopic variable, for example:

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

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T}$$

$$\left(\frac{\partial \ln K_{eq}}{\partial 1/T}\right)_P = -\frac{\Delta H^\circ}{R} \qquad \Delta H^\circ < 0 \text{ exothermic} \quad \Delta H^\circ > 0 \text{ endothermic}$$

Thermodynamics can also tell us what the final Equilibrium state (or "Terminal" state) will be of a system after we change or manipulate the walls:

Extent of a chemical Rxn, - Equilibrium constants

Changes of state, - phase Equilibria

It is important to recognize that the subject of Thermodynamics deals with <u>Macroscopic variables</u> and, hence, stands apart from any assumptions about the <u>microscopic</u> state of matter. Most of Thermodynamics was developed even before the atomic theory of matter was established.

Thermodynamic State of a System (Macroscopic State):

The Thermodynamic state of a system is specified by its <u>macroscopic properties</u>. Contrast this to classical or Quantum mechanics which defines the state of a system <u>microscopically</u> by specifying either position & momenta of all particles at a time, t:

$$\underset{\sim}{X}_1(t),\ \underset{\sim}{X}_2(t),\ \cdots \underset{\sim}{X}_N(t)\ ;\ \underset{\sim}{P}_1(t),\ \underset{\sim}{P}_2(t)\ \cdots \underset{\sim}{P}_N(t)$$

as in <u>classical mechanics</u> or through a time-dependent wavefunction in Quantum Mechanics:

$$\Psi(\underset{\sim}{X}_1, \underset{\sim}{X}_2, \cdots \underset{\sim}{X}_N, t)$$

which gives the probability distribution of all particles in a system at a time, t.
Whereas in classical or Quantum Mechanics, some 10^{23} coordinates are required to specify the state of a macroscopic system, in Thermodynamics only a few <u>macroscopic variables</u> are needed to specify the state of a system. It is the property of <u>Equilibrium states</u> that if only a few macroscopic variables of the system are specified, <u>all others</u> will be fixed.

Classification of Macroscopic Variables

<u>Extensive Variables</u>: quantities which are additive over constituent parts of the system, i.e.,

$U = U_1 + U_2$ (internal energy)

Examples: $U, V, \underset{\sim}{N}, M, C_p, H, G, A, S, \cdots$

Intensive Variables: thermodynamic quantities which are defined locally.

examples: $T, P, \rho, u, c_p, \Delta, \cdots$

intensive variables are the same (or vary continuously) over a homogeneous region (phase) of the system.
(note: vary discontinuously across phase boundaries)

→ Note that any Extensive variable can be made Intensive by normalizing with another Extensive variable. Typically this normalization is done through either the volume, V, or the Total number of moles, N.

e.g. $v \equiv V/N$ $\quad \Delta \equiv S/N$

$\rho \equiv M/V$ $\quad h \equiv H/N$

$u \equiv U/N$ $\quad s \equiv S/V$

$c_p \equiv C_p/N$ $\quad h \equiv H/V$

Types of Variables:

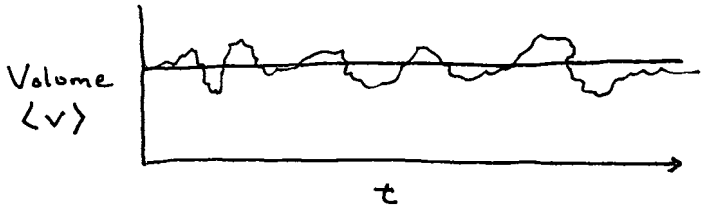
	Extensive		Intensive	Conjugate Field (intensive)	
Composition	$N_1, N_2, \cdots N_c$		$x_i \equiv N_i/N$	μ_i	(chemical potential)
	$N = \sum_{i=1}^{c} N_i$		(mole fraction)		
Mechanical	V	volume	$v \equiv V/N$	$-P$	pressure
	ℓ	Length		f	Tension
	$\mathcal{A}$	Area		γ	Surface Tension
	$V_0 \underset{\approx}{\varepsilon}$	STrain Tensor	$\underset{\approx}{\varepsilon}$	$\underset{\approx}{T}$	STress Tensor
	$\underset{\sim}{M}$	dipole moment	$\underset{\approx}{\chi}$	$\underset{\sim}{E}^{ext}$	Electric Field
	Q	electric charge		ϕ	Potential Difference
"Potentials"	U	internal Energy	$u \equiv U/N$		
	H	Enthalpy	$h \equiv H/N$		
	A	Helmholtz Free Energy	$a \equiv A/N$		
	G	Gibbs Free Energy	$g \equiv G/N$		
Entropy	S		$\Delta \equiv S/N$	T	Temperature

Derivative Properties	C_p	isobaric heat capacity	$c_p = C_p/N$
	C_v	isochoric heat capacity	$c_v = C_v/N$
	κ_T	isothermal compressibility	
	κ_S	Adiabatic Compressibility	
	α	volumetric Expansivity	
Transport Properties (Non-Thermo)	η	viscosity	
	D	Diffusion Coefficient	

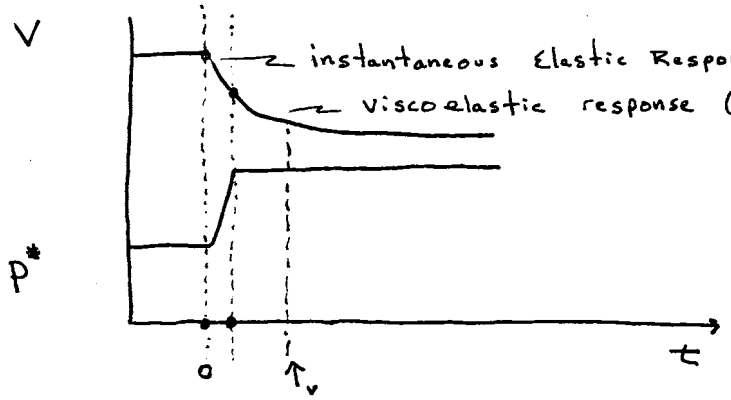
Measurement Timescale

The macroscopic properties of a system can be measured by Experiments. However, we have to be concerned with The Timescale of These measurements. The subject of Equilibrium Thermodynamics only deals with equilibrium (or Terminal) states. Thus, our measurements must be over Timescales That are sufficiently long That The measured quantities are time independent.

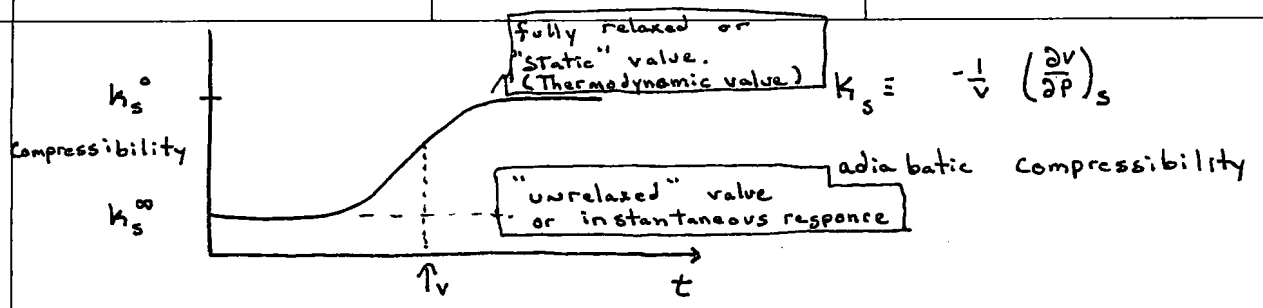
i.e.,



If we were able to measure the volume of a liquid on The pico second timescale we would observe something That depends on time as shown above. Thermodynamics deals with "average" quantitres. Typically, This is NOT a problem and our measurement scheme is Coarse Enough That it will do The averaging automatically. However, for viscous liquids, glesses, and Solids the microscopic relaxation times can be very long - and The System may take a very long time to reach Equilibrium or to give us an average picture. In these cases we must be very careful when we apply Thermodynamics. For example, consider the measurement of the adiabatic volume response of a viscous liquid to a change in pressure.



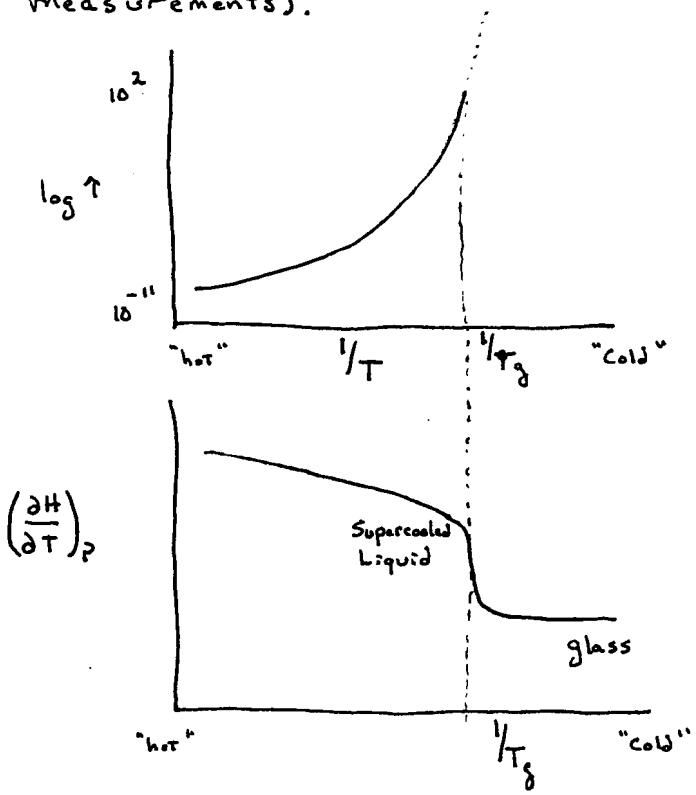
$\tau_v \equiv$ characteristic time for The volume relaxation of The liquid



For glycerol at room temp., $\tau_v \sim 10^{-6}$ sec, however, for methanol or water $\tau_v \sim 10^{-11}$ sec.

When τ exceeds typical experimentally accessible measurement times ($\tau > 10^2$ sec) then the material behaves as a glass.

Note that τ is a function of temperature. Typically τ increases as temperature decreases. If we can suppress nucleation of the crystalline phase at low temperature than the supercooled liquid will exhibit a <u>glass transition</u> when $\tau > 10^2$ sec (The relaxation time becomes longer than the typical laboratory timescales for calorimetric measurements).



Macroscopic State of a system is specified when ALL of the macroscopic variables are specified.

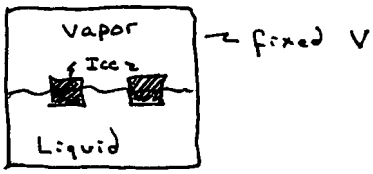
Fact of Experience, There exists:

Equilibrium States (Postulate I of H. Callen)

Equilibrium states have the property that all of the macroscopic variables are fixed when only a few are constrained. the number of variables which need to be specified depends on the number of fields acting on the system. Usually, we will treat the simplest of systems to formulate thermodynamic theory, we will typically only consider a pressure field. For each additional field we will require an additional variable to specify the state of the system.
For example, the macroscopic state of water is usually precisely specified if I know the T, P. No matter what path was taken to get to T & P all the intensive properties of water will be fixed at certain values if T & P are constrained. Two glasses of water have the same "density" properties if They are at The same T & P (at Equilibrium). To define all extensive properties as well we need T, P, N or for solutions $T, P, N_1, N_2 \cdots N_i$

Note

This does NOT always work.... if we have H_2O @ 0°C under its own vapor pressure, we will not know the relative abundances of ice, water, and vapor.



For example, if we add heat to the system we will melt Some of The ice and The relative abundances will change even though T, & P, & N are The Same! Thus, The System is Not completely Specified if we only specify T, P & N

However: Formally:

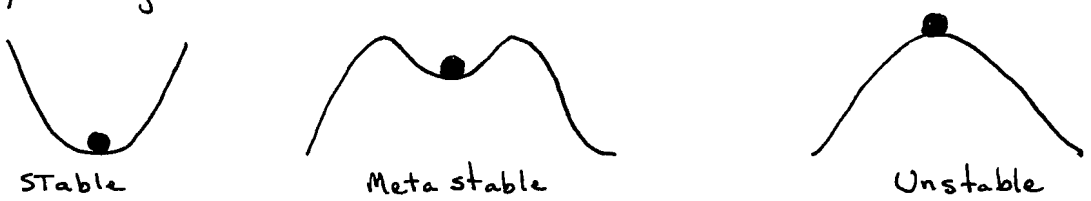
Postulate I (H. Callen): Equilibrium state of a simple System is completely specified (macroscopically) if we specify $U, V, N_1, N_2 \cdots N_i$

In more complex systems:
For each field acting on the system we need to include the conjugate Extensive variable. For example, in a solid under a general Stress Field, $\bar{\bar{T}}$, we must specify the entire strain tensor $V_0\bar{\bar{\Sigma}}$ instead of V alone.

Equilibrium States are stable with respect to all fluctuations. Fluctuations of density, pressure, entropy, etc... are always present in any system (these are ultimately what drive phase transitions, etc.) and the macroscopic properties will actually fluctuate randomly about their mean value. The magnitude of these fluctuations are typically hardly noticeable and our experiments will measure these average properties. Fluctuations, however, can become quite large, especially near critical points – critical opalescence.
Even with these large fluctuations the equilibrium state is stable and the system will always return to the average equilibrium state.

However there also exists;

Metastable States which can also be treated thermodynamically. These metastable states are locally stable. That is, they are stable with respect to small fluctuations. The existence of diamond at ambient conditions is a good example, or supercooled water. Water can exist at temperatures down to about -36°C provided the sample is extraordinarily clean without nucleation sites.
In mechanics these states can be represented on an Energy diagram as:



First Law of Thermodynamics

Much of Thermodynamics deals with the investigation of the physical and chemical changes that occur within a system as a result of a change (or manipulation) of the walls of the system. Consider a system that is initially at equilibrium. If we then change the walls – i.e., change the volume of the system, allow heat to flow into or out of the system, or add some additional chemical component to the system; Then changes in the system will be initiated and the system will try to re-establish a new equilibrium state in response to the manipulation of the walls.

Perhaps the most fundamental principle in evaluating changes within a system is the principle of Conservation of Energy. This principle is firmly rooted in the laws of physics which determine the behavior of particles on a microscopic level, and also embodies the essence of the First Law of Thermodynamics — which deals with processes in macroscopic systems.

⟹ All processes in nature, microscopic and macroscopic, are subject to an Energy conservation principle.

In order to apply the principle of conservation of Energy in Thermodynamic systems we have to keep Track of energy fluxes into and out of the system, i.e., Energy Exchange between the system & Surroundings.

For any process: $\Delta u = -\Delta u^*$

Δu: Change in Energy of system; $-\Delta u^*$: change in Energy of Surroundings

That is, for any <u>increase</u> in the Energy of the <u>system</u> There is a compensating and Equal <u>decrease</u> in the energy of the <u>surrounding</u>.

Thus, the only way that the internal Energy of a closed system can change is through a <u>flux</u> of Energy (Transfer) into or out of The system. Therefore, we have to keep track of these fluxes if we want to know the Δu of The System.

In general, we can identify two types of Energy fluxes in a closed system:

(Mechanical)		
	Work	w
	Heat	q

Work and heat are both Energy fluxes, they Simply represent two different modes of Energy Transfer.

Mechanical Work

$w \equiv$ Energy flux arising from the manipulation of the mechanical variables of the system.

i.e.,			$\delta w =$
	V	Volume	$-p^* dV$
	$\mathcal{A}$	Surface Area	$\gamma^* d\mathcal{A}$
	l	Length	$\mathcal{f}^* dl$
	Q	Electric Charge	$\phi^* dQ$
	M	Electric dipole moment	$E^* dM$

etc...

Heat ; $q \equiv$ any other Energy flux in a closed system is generally called heat. Energy transfer via heat occurs through incoherent atomic processes ; i.e., atomic collisions or radiative processes.

First Law

$$\Delta U = q + w$$

Equivalence of Heat & Work as Energy

Before the industrial revolution, heat & work were considered to be fundamentally different quantities. In fact, they were measured in different units.

Work : joules (J) $N\cdot m$
Erg (erg) $dyn\cdot cm$ (10^7 erg = 1 J)

Heat : Calorie (cal) unit of heat required to produce a $\Delta T = 1°C$ in water at 25°C

Joule demonstrated the equivalence of heat and work as Energy. They simply correspond to different channels for which Energy can be transferred. Once Energy, in any form, Enters a system this energy is redistributed among all of the different "aspects" of the system, i.e., kinetic Energy, potential Energy, vibrational, rotational, electronic, etc.. This redistribution is called "re equilibration".

After re-equilibration the system retains No Memory of how the energy was transferred, i.e., q or w cannot be determined, only ΔU is well defined.
Mathematically we say that U is a state variable but q & w are NOT.

Mechanical Work (Measurements)

Mechanical work in any process can be calculated from a knowledge of the External forces acting on the system and the change in the mechanical variables during the process.

In general, for an infinitessimal change in the systems mechanical variables,

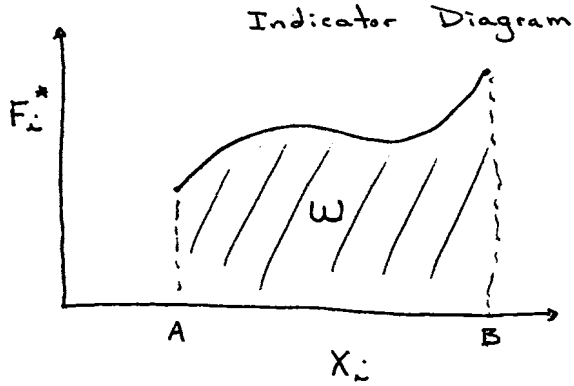
$$đw = \underset{\sim}{F}_i^* \cdot dX_i$$

- dX_i → mechanical variable displacement
- $\underset{\sim}{F}_i^*$ → conjugate External field variable
- $đw$ → differential change in work. (The slash on $đw$ is a reminder that w is NOT a state function, i.e., "inexact differential")

The Value of W is Path Dependent

$$W = \int_{\Gamma}^{B}_{A} \underset{\sim}{F}_i^* \cdot d\underset{\sim}{X}_i$$

Indicator Diagram



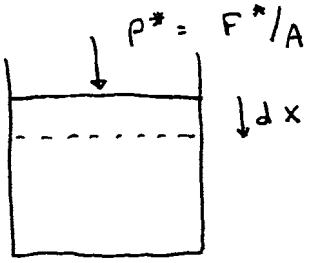
In general, to calculate W, we need to know the $\underset{\sim}{F}_i^* - X_i$ indicator diagram for the process.

Examples of Mechanical Work

Compression work

$-P^* dV$

dV: volume change; P^*: pressure

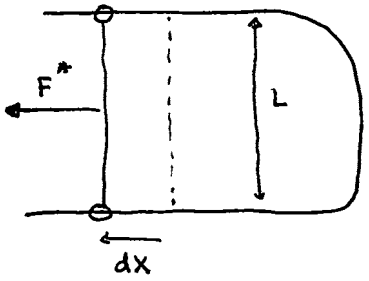


$$dW = F^* \cdot dx$$
$$= P^* A \, dx$$
$$= -P^* dV$$

Surface Tension work

$-\gamma \, d\sigma$

$d\sigma$: Area change; γ: Surface Tension



$$dW = F^* \cdot dx$$
$$= \frac{F^*}{L} \cdot L \, dx$$
$$= \gamma \, d\sigma$$

Linear Elastic Band

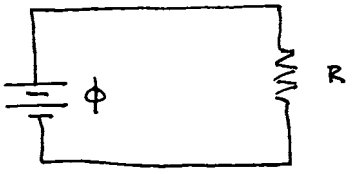
$f \cdot dl$

dl: length change; f: Tension

Electrical Work

$\phi \cdot dQ$

dQ: Electric change; ϕ: potential difference



ohm's law: $\boxed{\phi = iR}$

$$dW = \phi \cdot dQ$$
$$= iR \cdot dQ$$
$$W = iR \frac{dQ}{dt} \Delta\tau$$
$$= i^2 R \, \Delta\tau$$

gravitational work → $mg\,dh$

dh: height change; g: gravity; m: mass

Mathematics of Thermodynamics

A Quantity is a <u>state function</u> if the change in the quantity between two states is independent of the path taken connecting the two states.

A good example of a state function is "Elevation", h. Any point on a mountain has a well defined elevation. The difference in elevation between two points on the mountain is $(h_B - h_A) = \Delta h$ — it is the same regardless of how you get from state A → B. Thus, if you have some device that measures your change in height as you walk (i.e., an altimeter) it will record the same Δh regardless of the trail you take to get from A → B.

The number of calories your body burns to get from A → B depends on the path taken. So does the number of steps you take. These are examples of path-dependent quantities. They are NON-state functions.

The beauty of a state function is that it has a precise value (relative to some common reference) at ant point. This allows us to express this quantity as a <u>function</u> of other state variables.

Take the elevation, h, at any point on a map.

$h(x,y)$ specifies the height at any point x,y.

Regardless of the path between points A & B

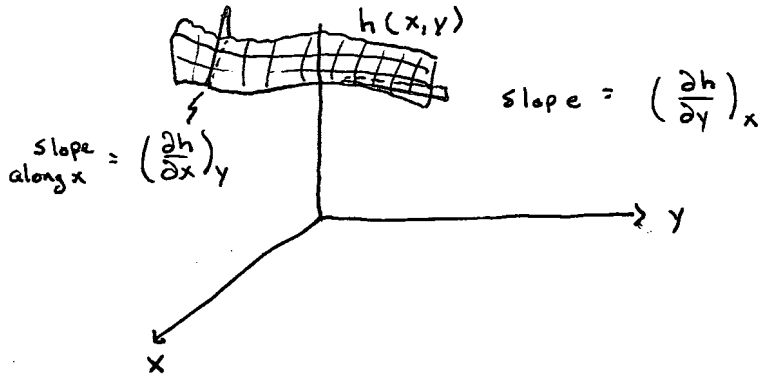
$$\Delta h = h(x_B, y_B) - h(x_A, y_A)$$

Mathematically, we can also define a <u>total differential</u>:

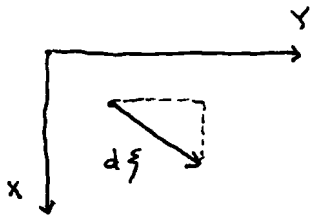
$$dh = \left(\frac{\partial h}{\partial x}\right)_y dx + \left(\frac{\partial h}{\partial y}\right)_x dy$$

where $\left(\frac{\partial h}{\partial x}\right)_y$ & $\left(\frac{\partial h}{\partial y}\right)_x$ are called <u>"partial derivatives"</u>

These partial derivatives represent tangent slopes of the h(x,y) surface at the specified x,y point in the specified direction:



X, Y projection



Slope along any arbitrary direction ; ξ

$$dh = \left(\frac{\partial h}{\partial x}\right)_y dx + \left(\frac{\partial h}{\partial y}\right)_x dy$$

$$\text{slope along } \xi = \frac{dh}{d\xi} = \left(\frac{\partial h}{\partial x}\right)_y \frac{dx}{d\xi} + \left(\frac{\partial h}{\partial y}\right)_x \frac{dy}{d\xi}$$

Exact Differentials

All state functions have the mathematical property that their Total differentials are <u>exact</u>.

Consider the differential expression for some quantity, h, with dependence on changes in x & y :

$$dh = M(x,y)\,dx + N(x,y)\,dy$$

The test for exactness is that :

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \qquad \left\{\begin{array}{l}\text{cross partials}\\ \text{are equal}\end{array}\right\}$$

Any differential expression that satisfies this relation is called an <u>exact differential</u> and must necessarily be a state function which can be written as $h(x,y)$.

The roundabout proof for this is that if h is a state function, its total differential is given by :

$$dh = \underbrace{\left(\frac{\partial h}{\partial x}\right)_y}_{M} dx + \underbrace{\left(\frac{\partial h}{\partial y}\right)_x}_{N} dy$$

Now inspect $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

$$\Rightarrow \quad \left(\frac{\partial}{\partial y}\left(\frac{\partial h}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial h}{\partial y}\right)_x\right)_y$$

$$\left(\frac{\partial^2 h}{\partial x \partial y}\right) = \left(\frac{\partial^2 h}{\partial y \partial x}\right)$$ mixed partial derivatives.

The equality of the mixed partial derivatives embodies the principle of path independence. Qualitatively, if we traverse dx then dy, the dh that we measure will be the same as that for a path where we traverse dy first then dx. Thus, as long as we end up at the same point, Δh is independent of path.

Mathematical Relations

Recall, for <u>Equilibrium States</u> if a small subset of the macroscopic variables are specified then all others will be specified. That is, we only need to specify a few of the macroscopic variables to completely define the thermodynamic state of the system when it is at equilibrium. This leads to a tremendous simplification and means that of the enormous number of macroscopic variables only a few of them are actually independent variables (in the mathematical sense).

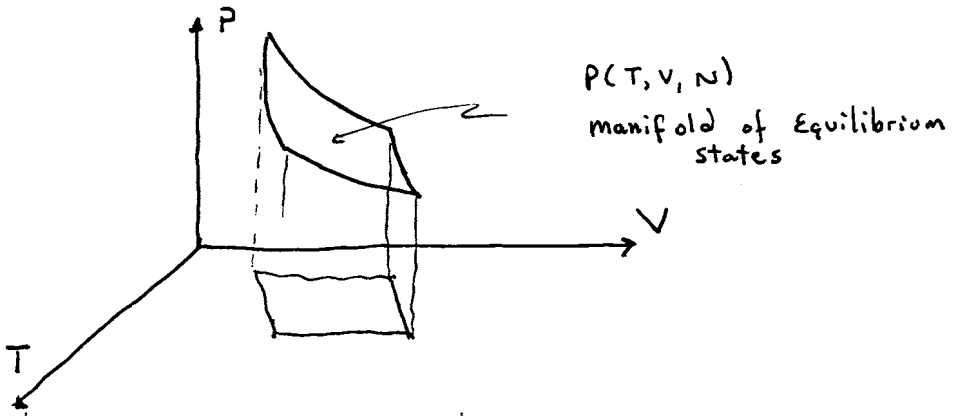
For a simple system, i.e., one with only a pressure field acting on the system and only one composition variable, there are only 3 independent macroscopic variables (see Callen's postulate I).

Typically, <u>it is up to us to choose which 3 variables we will use to define the state of the system.</u> This choice is somewhat arbitrary, although some sets are more useful than others. The choice of independent variables is <u>usually made out of convenience</u>.

Consider a simple <u>homogeneous</u> system, for example, a fluid where we choose T, V & N as the <u>independent variables</u>. Any other macroscopic property of the equilibrium states of this fluid can be expressed as a function of these three variables:

$P(T, V, N)$
$H(T, V, N)$
$S(T, V, N)$
$C_p(T, V, N)$
etc.

} "<u>Functions of State</u>" (only valid for Equilibrium states.)



The fact that for Equilibrium States there are only a small number of independent macroscopic variables, means that <u>all</u> of the macroscopic variables can be related to each other mathematically. This leads to a tremendous simplification in the thermodynamics of Equilibrium. (which to the student may not be seen as a simplification since now all thermodynamic quantities can be related to each other!)

Before we continue our thermodynamics we need to review the mathematics of multivariables:

Total Differential

$P(T, V, N)$ 1 component simple system.

$$\Rightarrow dP = \left(\frac{\partial P}{\partial T}\right)_{V,N} dT + \left(\frac{\partial P}{\partial V}\right)_{T,N} dV + \left(\frac{\partial P}{\partial N}\right)_{T,V} dN$$

$U(S, V, N_1, N_2)$ 2 component simple system.

$$\Rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N_1}\right)_{S,V,N_2} dN_1 + \left(\frac{\partial U}{\partial N_2}\right)_{S,V,N_1} dN_2$$

Chain Rule (change of Variables)

Suppose we expand dU with T & V as our independent variables (so N is fixed → closed system):

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

Now we wish to make a change of our independent variables to T & P. To do this we need to expand dV:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

Then substitute into eqn for dU:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right]$$

Rearranging:

$$dU = \left[\left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP$$

Note that at the onset, we could have expanded dU in terms of T & P

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

Thus:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

i.e.,

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

These are 2 examples of The <u>Chain Rule</u>.

Note: The first example we are changing the variable held fixed & in the second we are keeping the same variable fixed.

A Quick way to Remember These is that if we start from the Total differential:

i.e., $$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

we can divide through be $\left(\frac{1}{\partial T}\right)_P$

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \underbrace{\left(\frac{\partial T}{\partial T}\right)_P}_{=1} + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow \boxed{\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P}$$

or, we can divide through by $\left(\frac{1}{\partial P}\right)_T$

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial T}\right)_V \underbrace{\left(\frac{\partial T}{\partial P}\right)_T}_{=0 \text{ (since } T \text{ is held fixed)}} + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

$$\Rightarrow \boxed{\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P} \quad ?$$

We can use the same scheme to prove the cyclic rule:

Consider $T(P, H)$:

$$dT = \left(\frac{\partial T}{\partial P}\right)_H dP + \left(\frac{\partial T}{\partial H}\right)_P dH$$

divide through by $\left(\frac{1}{\partial P}\right)_T$:

$$\left(\frac{\partial T}{\partial P}\right)_T = \left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial P}\right)_T + \left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T$$

$\left(\frac{\partial T}{\partial P}\right)_T = 0$ $\qquad$ $\left(\frac{\partial P}{\partial P}\right)_T = 1$

$$0 = \left(\frac{\partial T}{\partial P}\right)_H + \left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T$$

rearranging:

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T}$$ cyclic Rule

One final rule we need is the reciprocal theorem:

i.e.,

$$\boxed{\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}}$$

Using the reciprocal theorem, we can rearrange the cyclic rule:

$$\boxed{-1 = \left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H}$$

Notice that only $T, P, \& H$ appear as variables!

One formula to note, (we will prove it later when we introduce Maxwell Relations)

$$dU = TdS - PdV$$

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

$\downarrow$ maxwell relation

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P}$$

Reversible Processes

If the manipulation of the walls of the System is done slow enough then the system will always be infinitessimally close to an Equilibrium State during the process. This type of process is called a "reversible" process since the system will traverse through the same set of Equilibrium States in both the forward or reverse directions.

In reversible processes, the system's intensive field variables are in mechanical equilibrium with the external fields.

i.e., $P^* = P(T, V, N)$ (NOTE: Assumption that we can ignore surface tension effects)

P^*: External Pressure

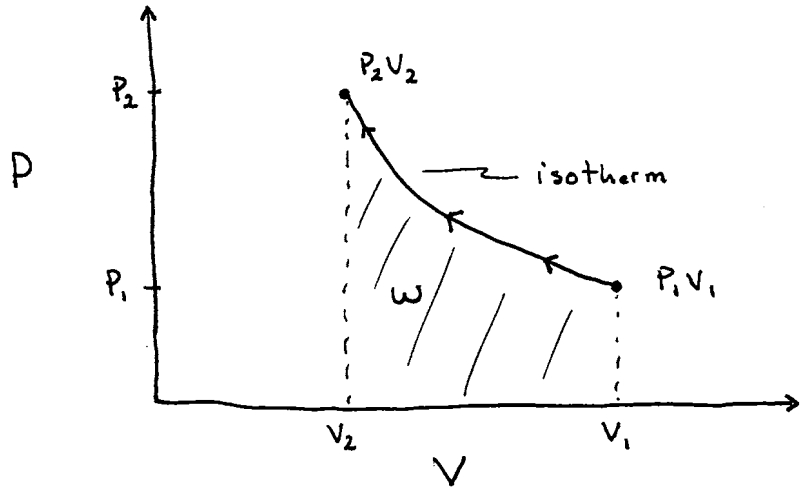
$P(T, V, N)$: System pressure (State Variable for Equilibrium state)

$$\Rightarrow \quad \underbrace{w = -\int_{V_1}^{V_2} P^* \, dV}_{P} = \underbrace{-\int_{V_1}^{V_2} P(T, V, N) \, dV}_{P_{rev}}$$

Valid for All processes — Valid only for Reversible processes

The beauty of reversible processes, is that instead of needing to know P^* along the path, we can use the System State variable, P.

Example: isothermal compression/expansion of an ideal gas:



$$w = -\int_{V_1}^{V_2} P \, dV = -\int_{V_1}^{V_2} \frac{NRT}{V} \, dV$$

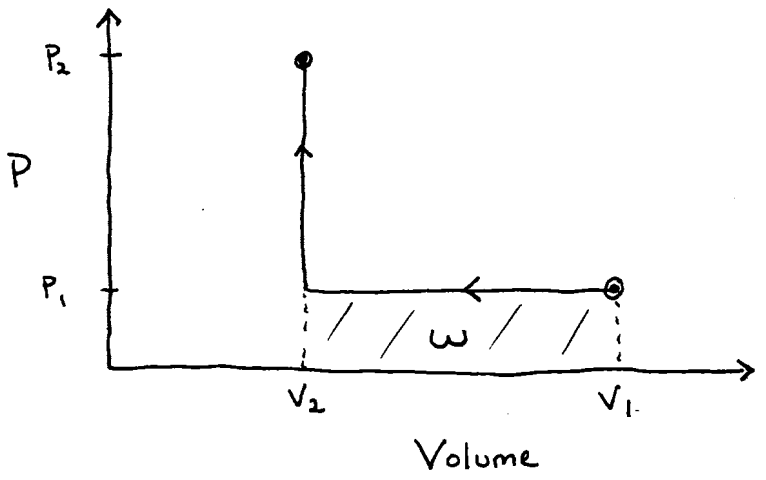
along an isothermal path, T is fixed and so we have:

$$w = -NRT \int_{V_1}^{V_2} \frac{dV}{V} = -NRT \ln V_2/V_1$$

$$w_{rev} = -NRT \ln\left(\frac{V_2}{V_1}\right) \qquad \text{ideal gas}$$

Compare this value for w_{rev} to another reversible process where the system traverses from

$$P_1V_1 \longrightarrow P_1V_2 \longrightarrow P_2V_2$$



$$w = -\int_{P_{rev}} P\,dV = -P_1 \int_{V_1}^{V_2} dV = -P_1(V_2 - V_1)$$

This is quite a bit smaller than the work done on the system in the previous example. This emphasizes the point that ΔU is the same for each process (both processes start out at P_1V_1 and end at P_2V_2. Since U is a state variable, $U_2 - U_1$ is the same <u>regardless of path</u>).

The point is that the energy difference between two states A & B is a fixed quantity, ΔU, regardless of the path taken. However, the work done in a process which takes state A → B <u>depends on the path</u>. In general, w will be different for different paths.

Adiabatic Accessibility

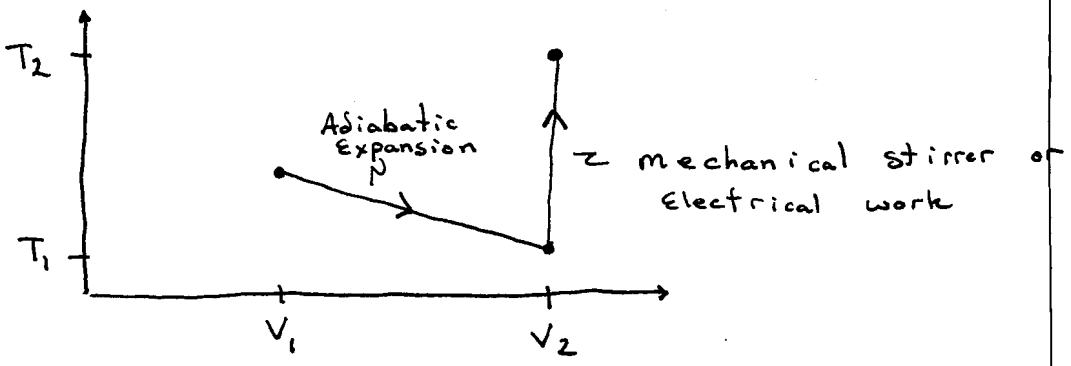
We can directly measure mechanical work if we know the indicator diagram (F^*, X_i) of the process. However, how do we measure the quantity of heat transferred in a process?

This can only be done indirectly via the principle of <u>Adiabatic accessibility</u>. That is, if we know ΔU for the process then we can obtain q from the relation:

$$q = \Delta U - W \qquad \text{(for a specific process)}$$

The principle of adiabatic accessibility states that we can <u>always</u> connect two different Equilibrium States via an <u>adiabatic</u> process where only mechanical work is done.

Consider two Equilibrium States of a system $U_1(T_1, V_1)$ & $U_2(T_2, V_2)$



Note, however, that adiabatic accessibility does <u>NOT</u> ensure that the states A & B can be connected by an adiabatic process in Either direction:

A $\xrightarrow{\text{Adiabatic}}$ B

<u>OR</u>

A $\xleftarrow{\text{Adiabatic}}$ B

But Not Necessarily A $\overset{\text{Adiabatic}}{\rightleftharpoons}$ B

This limitation or <u>Assymetry</u> in the directionality of adiabatic processes embodies the 2nd law of thermodynamics → which we will discuss later.

Adiabatic accessibility thus ensures that we can always measure q of any process through Some mechanical calibration.

$$q = \Delta U - W$$

q: path Dependent

W: Path dependent (Mechanical)

ΔU: Independent of Path. Can be measured from Some adiabatic process

Isochoric Process

The first-law: $dU = \delta q + \delta w$

$= \delta q - P^* dV + \delta w_e$

where $-P^* dV$ is the comp./Exp. work & δw_e is any additional (extra) work terms.

After any isochoric process, where No Extra work is performed ($\delta w_e = 0$), Then

$$dU = \delta q_V$$ ← subscript is added here To remind us That The process is isochoric

Non-differential processes, we can also write:

$$\Delta U = Q + W$$

under fixed P^*, we have,

$$\Delta U = Q - P^* \Delta V + W_e$$

↳ "Extra" work term

In any process, if $\Delta V = 0$ (i.e., $V_1 = V_2$) and No extra work is done ($W_e = 0$)

$$\Rightarrow \Delta U = Q_V$$ {we can relate the heat absorbed by the system to its Energy change}

The heat adsorbed by a system in an isochoric process can be related To the temperature rise & the isochorrc heat capacity of the system In general, we can Expand any state function in terms of any complete Set of independent variables: The internal energy, U, for a simple system, single-component, single-phase with no external fields other Than pressure, U can be expanded in a set of 3 independent variables:

$$U(T,V,N) \Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV + \left(\frac{\partial U}{\partial N}\right)_{T,V} dN$$

for fixed N, $dN = 0$ $\Rightarrow$ $dU = \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV$ (fixed N)

define the material property, $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{V,N}$ (isochoric heat capacity)

$$\Rightarrow \quad \boxed{dU = C_V\,dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV \qquad \text{fixed } N}$$

$$\boxed{\text{isochoric processes: } \qquad dU = C_V\,dT}$$

The isochoric heat capacity, C_V, can be related to heat flow in an isochoric process when <u>No</u> extra work is performed

$$dU = C_V\,dT = \text{đ}q_V$$

or

$$\frac{\text{đ}q}{dT} = C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

C_V is a material coefficient which expresses the relation between the heat adsorbed in a system at fixed volume to its temperature rise.

C_V is itself a state function which can also be expressed as a function of independent variables:

$$C_V = C_V(T, P, N)$$

C_V is an <u>Extensive Variable</u>. We can define an intensive quantity,

$$c_V \equiv \bar{C}_V \equiv \frac{C_V}{N}$$

Isobaric Processes : (Enthalpy, H, State function)

We define a new state function called :

> "Enthalpy", $H \equiv U + PV$ (General Definition)
>
> P ↓ System pressure

H is a state function since $U, P, \& V$ are all state functions.

Consider any process (reversible or irreversible) where the initial & final pressures of the System are equal to a fixed external pressure, P^*.

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P^* \Delta V$$

Now apply the 1st-Law :

$$\Delta H = Q - P^* \Delta V + w_e + P^* \Delta V$$

$$= Q + w_e$$

if $w_e = 0$,

> $\Rightarrow \Delta H = Q_p$
>
> for Any process provided $P_1 = P_2 = P^* =$ constant & $w_e = 0$

The heat adsorbed by a system in any process where the External Pressure is fixed and $P_1 = P_2 = P^*$ is given by ΔH (provided $w_e = 0$).

Differential Processes :

$$dH = dU + d(PV) = dU + PdV + VdP$$

from the 1st-law :

$$dH = dq - P^* dV + PdV + VdP + dw_e$$

$$= dq - (P^* - P)dV + VdP + dw_e$$

> if $P = P^* =$ constant & $dw_e = 0$
>
> $\Rightarrow dH = dq_p$

Since H is a state function, we can expand its total differential in any convenient set of variables. If we choose $H(T, P, N)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P,N} dT + \left(\frac{\partial H}{\partial P}\right)_{T,N} dP + \left(\frac{\partial H}{\partial N}\right)_{T,P} dN$$

for fixed N, $dN = 0$

$$\Rightarrow dH = \left(\frac{\partial H}{\partial T}\right)_{P,N} dT + \left(\frac{\partial H}{\partial P}\right)_{T,N} dP \qquad N \text{ fixed}$$

We <u>define</u> the material property;

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_{P,N} \qquad \text{"isobaric" Heat Capacity}$$

$$\Rightarrow dH = C_P\, dT + \left(\frac{\partial H}{\partial P}\right)_{T,N} dP \qquad \text{fixed } N$$

for <u>isobaric processes</u>, $dH = C_P\, dT$

Therefore, if $P = P^* = \text{constant}$ & $dw_e = 0$

$$\Rightarrow dH = C_P\, dT = đq_P$$

or

$$\frac{đq_P}{dT} = C_P \equiv \left(\frac{\partial H}{\partial T}\right)_{P,N}$$

C_P is similar to C_V except that it is a measure of the amount of heat required to raise the temperature of a system by $1°K$ <u>at constant pressure</u> NOT at constant volume.

the general relations,

$\Delta U = Q_V$ any isochoric process ($\& \; W_e = 0$) ($V_1 = V_2$)

$\Delta H = Q_P$ any isobaric process ($\& \; W_e = 0$) ($P_1 = P_2 = P^*$)

are extremely useful since they provide important connection between calorimetric data (heat flow measurements) and thermodynamic state functions.

the utility of U & H are NOT limited to isochoric or isobaric processes, changes in these functions can certainly be calculated regardless of whether $\Delta V = 0$ or $\Delta P = 0$

i.e., $\Delta H \equiv \Delta U + \Delta(PV) = U_2 - U_1 + P_2 V_2 - P_1 V_1$

also

$$dH = C_P \, dT + \left(\frac{\partial H}{\partial P}\right)_{T,N} dP$$ fixed N, single phase

$$dU = C_V \, dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV$$ fixed N, single phase

"Sensible" Heat

The enthalpy difference $(H_T - H_{298})$ of a substance at constant pressure is termed the "Sensible" Heat.

$$H_T - H_{298} = \int_{298}^{T} C_p(T')\, dT'$$

often, the C_p of a substance is expressed by an Equation of the form:

$$C_p(T) = a + bT - c/T^2$$ Empirical Eqn.

(This eqn. is typically valid only <u>above</u> 298k)

If a phase transition occurs in the substance, heat may be absorbed or released as a consequense of the transition without resulting in a temperature change. This is called the "Latent Heat" & must be accounted for to obtain the total Sensible Heat.

One of the simplest examples would be that of melting. At the melting point a substance will adsorb heat without an increase in temperature. The heat adsorbed merely transforms a portion of the sample from a solid to a liquid.

Thermo Chemistry - Applications of the 1st-Law to Chemical Rxn.

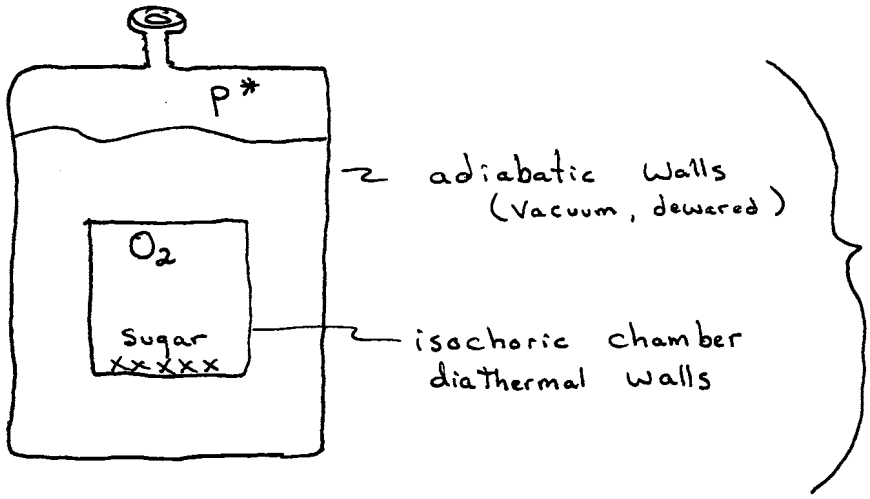
We showed before that under certain processes the heat adsorbed or evolved, Q, in a change of state could be related to the ΔU or ΔH between the initial & final states, regardless of whether the process was reversible or irreversible:

$Q = \Delta U$	isocheric process : No Work	
$Q = \Delta H$	isobaric process : $P_1 = P_2 = P^*$	No other work

<u>Thermochemistry</u> deals with the heat associated with chemical reactions. Measurements of the heat evolved or absorbed in chemical reactions can be obtained from calorimetric measurements. These measurements provide important data on the ΔU & ΔH between different states of matter.

$Q < 0$	ExoThermic (heat given off from system)
$Q > 0$	EndoThermic (heat absorbed into system)

Isochoric Calorimeter (Bomb Calorimeter)



$\Delta H \neq 0$ Since $P_2 \neq P_1$

first-law : $\Delta u = \cancel{Q}^{=0} + w = -P^* \Delta V^{cal}$

$$u^{cal}(T_2, P^*) + u^{prod}(T_2, V) - u^{cal}(T_1, P^*) - u^{react}(T_1, V) = -P^* \Delta V^{cal}$$

$$\left[u^{cal}(T_2, P^*) + P^* V^{cal}(T_2, P^*)\right] - \left[u^{cal}(T_1, P^*) - P^* V^{cal}(T_1, P^*)\right] + u^{prod}(T_2, V) - u^{react}(T_1, V) = 0$$

$$H^{cal}(T_2, P^*) - H^{cal}(T_1, P^*) + u^{Prod}(T_2, V) - u^{react.}(T_1, V) = 0$$

$$C_p^{cal}(T_2 - T_1) + C_v^{prod}(T_2 - T_1) + u^{prod}(T_1, V) - u^{react}(T_1, V) = 0$$

$$u^{Prod}(T_1, V) - u^{react}(T_1, V) = -\left[C_p^{cal} + C_v^{Prod}\right](T_2 - T_1)$$

$$\boxed{\Delta u_{rxn}(T_1, V) = -\left[C_p^{cal} + C_v^{prod}\right](T_2 - T_1)}$$

Also obtain ΔH if we know the change in number of moles of gas :

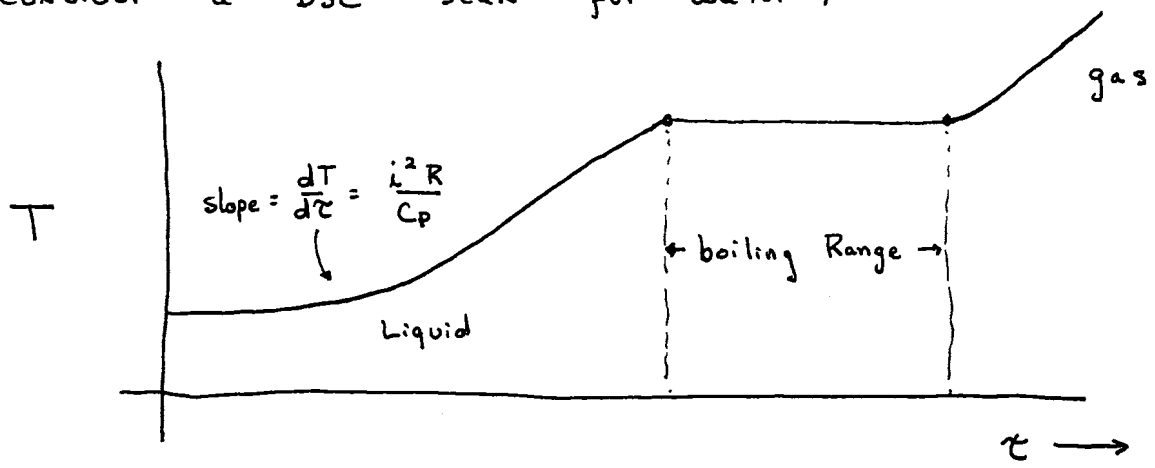
$$\Delta_r H = \Delta_r u + \Delta_r PV$$

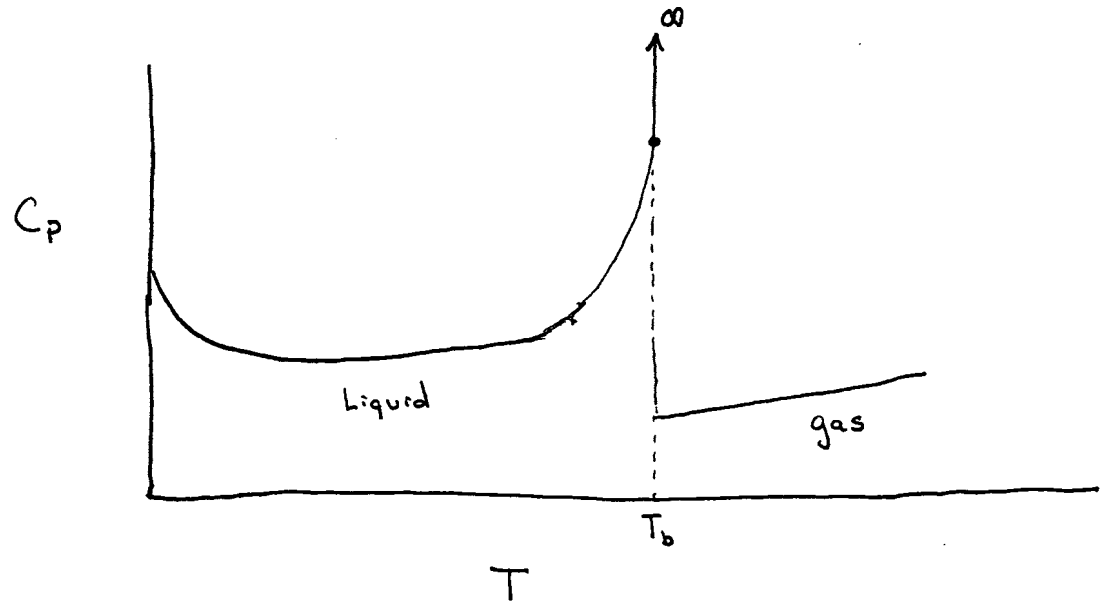
(ignore the volume of any solid/liquids)

In differential Scanning Calorimetry, The heat capacity of the Calorimeter is essentially eliminated leaving:

$$C_p(T) = \frac{i^2 R}{\left(\partial T / \partial \tau\right)_p}$$

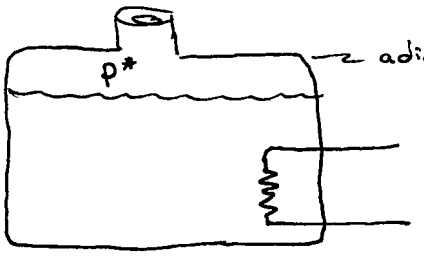
Consider a DSC scan for water;





Calorimetric Determinations of Heat Capacities

C_p, isobaric heat capacity



$$dw_e = \varepsilon i\, dt = i^2 R\, dt$$

Resistive Heater ($\varepsilon = iR$)

$P_1 = P_2 = P^*$, $Q = 0$ $\Rightarrow$ $\Delta H_{Total} = w_e$

$$\underbrace{H_T - H_{298}}_{\text{Enthalpy change of Substance (Sensible Heat)}} + \underbrace{H_{cal,T} - H_{cal,298}}_{\text{Enthalpy change of Calorimeter}} = i^2 R\, t$$

t: Total time heater is "on"

$$H_T - H_{298} = i^2 R\, t - (H_{cal,T} - H_{cal,298})$$

Take the derivative w/ respect to (w.r.t) Temp.

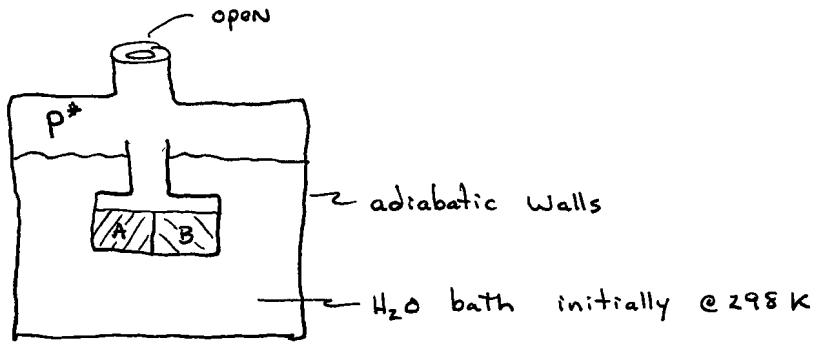
$$\left(\frac{\partial H_T}{\partial T}\right)_P = i^2 R \left(\frac{\partial t}{\partial T}\right)_P - \left(\frac{\partial H_{cal,T}}{\partial T}\right)_P$$

$$\boxed{C_p(T) = \frac{i^2 R}{\left(\partial T/\partial t\right)_P} - C_{p,cal}(T)}$$

Calorimetric Measurements of Heats of Reaction

isobaric calorimeter $\quad P_1 = P_2 = P^*$

Consider an adiabatic calorimeter where the reaction occurs at fixed P^*.



Adiabatic $\quad Q = 0$ for reaction species + calorimeter

$P_1 = P_2 = P^*$

$W_e = 0$

$\Big\} \Delta H_{Total} = 0$

$\longrightarrow$ if the rxn goes to completion,

$$H_{prod}(T, P^*) + H_{cal}(T, P^*) - H_{react}(298, P^*) - H_{cal}(298, P^*) = 0$$

$$H_{prod}(298, P^*) + C_{p,prod}(T-298) + H_{cal}(298, P^*) + C_{p,cal}(T-298)$$
$$- H_{react}(298, P^*) - H_{cal}(298, P^*) = 0$$

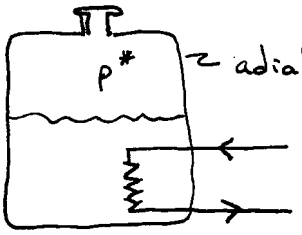
$$H_{prod}(298, P^*) - H_{react}(298, P^*) = -\left[C_{p,prod} + C_{p,cal}\right](T-298)$$

$$\Rightarrow \Delta H_{rxn}(298, P^*) = -\left[C_{p,prod} + C_{p,cal}\right](T-298)$$

Sensible Heat of reaction.

Measurement of C_V & C_p

As discussed earlier, There is <u>no direct way</u> to measure the heat flow into or out of a system. However, we can use the <u>adiabatic accessibility principle</u> (p. 19) To obtain Q for any process. One method of measuring C_p is to use electrical work to raise the temperature of a system at constant P. (similiar to p. 28)



adiabatic calorimeter ($dq = 0$) $P = P^*$ isobaric

$$dw_e = i^2 R\, dt$$

$$dH = dU + d(PV) = dU + P\,dV + V\,dP$$

from the 1st law;

$$dH = \cancel{dq}^{0} - P^*\,dV + dw_e + P\,dV + V\,dP$$

$$\boxed{dH = dw_e = i^2 R\, dt \qquad \text{adiabatic, isobaric} \quad P = P^*}$$

Now we can expand dH in terms of T & P

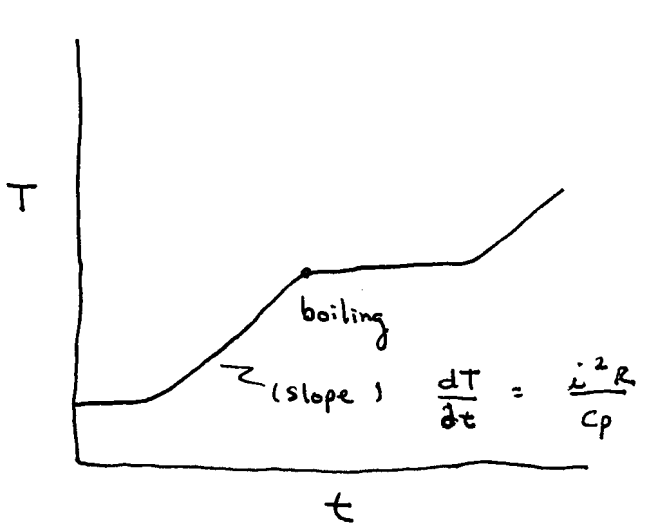
$$dH = C_p\,dT + \left(\frac{\partial H}{\partial P}\right)_T \cancel{dP}^{\to 0} = i^2 R\, dt$$

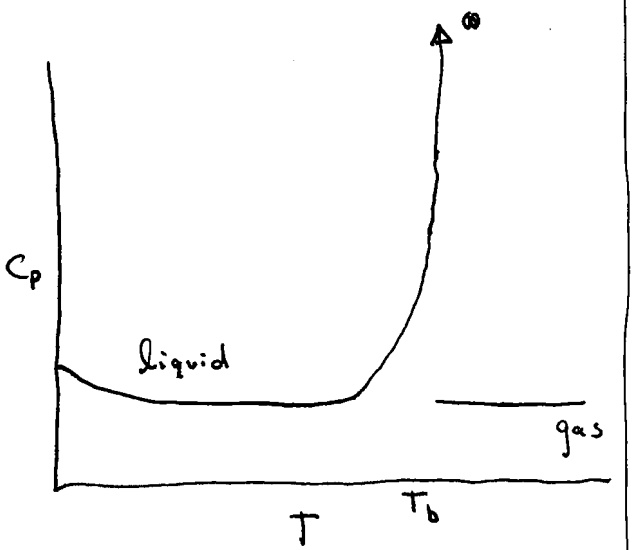
$$dH = C_p\,dT = i^2 R\, dt$$

or

$$\boxed{i^2 R \frac{dt}{dT} = C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p}$$

adiabatic, isobaric, $P = P^*$





Relation between C_p & C_V

Recall : $dH = dU + d(PV)$

$$dH = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV + VdP$$

Now taking: $\;/\partial T)_P$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_V \underbrace{\left(\frac{\partial T}{\partial T}\right)_P}_{1} + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P + V\underbrace{\left(\frac{\partial P}{\partial T}\right)_P}_{0}$$

$$\Rightarrow \boxed{C_p - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P}$$

We can identify two terms which contribute to the difference in C_p & C_V — both result from thermal Expansion of the system $(\partial V/\partial T)_P$.

① $P\left(\frac{\partial V}{\partial T}\right)_P$ represents <u>Expansion work</u> done by the system per unit increase in T.

② $\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$ represents the Energy required to Separate the molecules (against the intermolecular attractive forces) per unit increase in T.

We can express $C_p - C_V$ in a different form by noting:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{(prove later)}$$

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

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

$$\boxed{C_p - C_V = \frac{TV\alpha^2}{K_T}}$$

where $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ Note, $\alpha^2 > 0$

$K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ $K_T > 0$ } positive Definite

Therefore, $\boxed{C_p - C_V > 0 \quad \text{always}}$

Example: ideal gas:

$$P = \frac{NRT}{V} \qquad \text{or} \qquad V = \frac{NRT}{P}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{NR}{V} = \frac{P}{T}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{NR}{P} = \frac{V}{T}$$

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

$$\boxed{C_P - C_V = NR \qquad \text{for an ideal gas}}$$

Thermochemistry : Application of the 1st-law to Chm. Rxn.

Recall that under certain processes the heat adsorbed or Evolved, Q, in a change of state can be related to the ΔU or ΔH between the initial & final States regardless of whether the process was reversible or irreversible.

$Q = \Delta U$	isochoric processes No work $(w=0)$
$Q = \Delta H$	$P_1 = P_2 = P^*$ constant (isobaric) No Extra work $(w_e = 0)$

Thermochemistry deals with the heat associated with chemical reactions. Measurements of the heat Evolved or absorbed in chemical reactions can be obtained from calorimetric measurements. These measurements provide important data on the ΔH & ΔU between different states of matter.

Classification of Rxns:

- Exothermic : $(Q < 0)$ Heat Evolved due to rxn. Temperature rises in adiabatic calorimeter.
- EndoTherimic : $(Q > 0)$ Heat adsorbed due to rnx. Temperature lowers in adiabatic rxn.

To discuss the thermodynamics of chemical rxns it is convenient to represent a chemical reaction by an Equation:

"Mass Balance Relation"

$$0 = \sum_{i=1}^{s} \nu_i A_i$$

The Sum over i is over all substances (s) involved in The rxn.

where: $\nu_i \equiv$ Stoichiometric Coefficient of a rxn. $\nu_i > 0$ products, $\nu_i < 0$ reactants

$A_i \equiv$ molecular component of Substance involved in rxn.

Example :

Consider the balanced rxn :

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightleftharpoons H_2O(\ell)$$

By convention this rxn would be written :

$$0 = -1\, H_2(g) - \tfrac{1}{2} O_2(g) + 1\, H_2O(\ell)$$

We define the Extent of reaction, ξ.

$$d\xi \equiv \frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \cdots = \frac{dN_s}{d\nu_s}$$

where ξ : "Extent of Reaction"

i.e.

$$N_i(\xi) = N_i^0 + \nu_i \xi$$

N_i^0 : initial moles of i^{th} substance

$N_i(\xi)$: moles of i^{th} substance for some ξ

Note: ξ is an Extensive quantity with units of moles.

ξ is defined by the balanced chemical rxn that we write down.

Consider the two valid ways of writing down the reaction :

$H_2(g) + \tfrac{1}{2} O_2(g) \rightleftharpoons H_2O(g)$ if, $\Delta\xi = 1$, $\Delta N_{H_2O} = 1$

$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ if, $\Delta\xi = 1$, $\Delta N_{H_2O} = 2$

At fixed T & P, the enthalpy of the system depends on the extent of the reaction.

$$H(T, P, N_1, N_2, N_3, \cdots, N_S)$$

In general:

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P, N_i \cdots N_S} dT + \left(\frac{\partial H}{\partial P}\right)_{T, N_i \cdots N_S} dP + \sum_{i=1}^{S} \left(\frac{\partial H}{\partial N_i}\right)_{T,P,N'} dN_i$$

at fixed T & P

$$dH = \sum_{i=1}^{S} \left(\frac{\partial H}{\partial N_i}\right)_{T,P,\underline{N}'} dN_i$$

$\underline{N}'$ ≡ all N_j fixed except N_i

$$= \sum_{i=1}^{S} \bar{H}_i \, dN_i \qquad \text{where } \bar{H}_i \equiv \left(\frac{\partial H}{\partial N_i}\right)_{T,P,\underline{N}'}$$

"partial molar enthalpy"

if N_i only change through a chemical rxn,

$$dN_i = \nu_i \, d\xi$$

$$dH = \sum_{i=1}^{S} \nu_i \bar{H}_i \, d\xi = \Delta_r H \, d\xi$$

where, $\Delta_r H \equiv \sum_{i=1}^{S} \nu_i \bar{H}_i$ "Enthalpy of Reaction"

Note:

$$\Delta_r H = \left(\frac{\partial H}{\partial \xi}\right)_{T,P} \approx \left.\frac{\Delta H}{\Delta \xi}\right|_{T,P \text{ fixed}}$$

if the system is very large so that $\Delta\xi = 1$ mol makes essentially no change in the composition of the system then we can write:

$$\Delta_r H = \Delta H / 1 \text{ mol}$$

$\Delta_r H$ is a "molar" quantity (i.e., J/mol)

Standard States

The large body of thermochemical data of reactions is Tabulated for reactions in which the reactants & products are in Their Standard States. When Substances are in Their Standard state, we use the Superscript "°".

$$\Delta_r H^\circ(T) = \sum_{i=1}^{s} \nu_i \bar{H}_i^\circ(T)$$

Enthalpies of standard states are only functions of Temperature (T).

By definition:

- The standard state of gas (g) is the pure gas in the hypothetical ideal gas state at a pressure of 1 bar ($P^\ominus$) and at The temperature of interest, T.
- The Standard State of a liquid (ℓ) is the pure liquid at $P^\ominus$ & T.
- The standard state of a solid (s) is the pure crystalline substance at $P^\ominus$ & T
- The standard state of a dilute solution is typically given as an ideal solution at unit molality, m (moles solute / kg Solvent) at $P^\ominus$ & T.

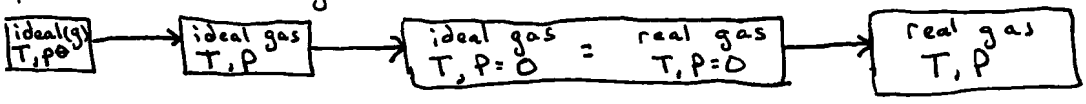
By Convention:

$(aq) \equiv$ undissociated species

$(a_i) \equiv$ Completely dissociated Electrolyte

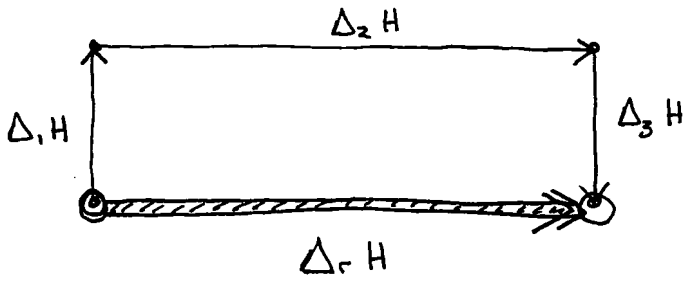
$(a_q) \equiv$ aqueous solvated Species
(This useage is now obsolete but still used!)

Note That for gases, The standard state is not chosen to be the actual gas state but is a "hypothetical ideal gas state" of The same gas at $P^\ominus$. In this hypothetical state the interactions between the gas molecules are neglected. This hypothetical state is a very convenient reference state for the gas. The temp. dependent properties of the ideal gas state can be easily calculated from spectroscopic data on the vibrational & rotational Energy levels of The molecules.
Corrections from the Ideal gas state at $(T, P^\ominus)$ to the actual state of The real gas at (T, P) must ultimately be made. This correction can be made if The EoS of the real gas is known.



Hess' Law

Since H is a <u>state function</u>, we can calculate $\Delta_r H$ by combining Thermochemical reactions in an algebraic sense:



$\Delta_r H: \Delta_1 H + \Delta_2 H + \Delta_3 H$

This makes it possible to determine the $\Delta_r H$ for reactions that cannot be easily measured. For example, Consider the partial combustion of graphite to Carbon Monoxide:

$$C_{(graphite)} + \tfrac{1}{2} O_{2(g)} \rightleftharpoons CO_{(g)} \qquad \Delta_r H = ?$$

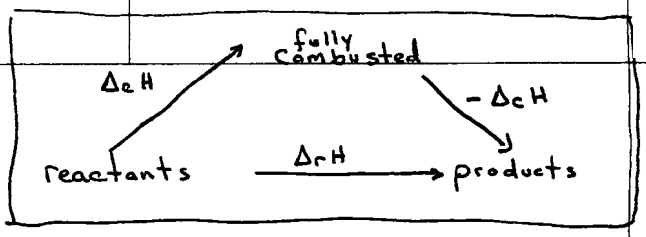
We can obtain this enthalpy of reaction ($\Delta_r H$) by combining the Enthalpies of reactions for the complete combustion of graphite to CO_2 & the combustion of CO To CO_2:

$$C_{(graphite)} + O_{2(g)} \rightleftharpoons CO_{2(g)} \qquad \Delta_r H = -393 \text{ kJ}$$

$$CO_{2(g)} \rightleftharpoons CO_{(g)} + \tfrac{1}{2} O_{2(g)} \qquad \Delta_r H = 282 \text{ kJ}$$

$$C_{(graphite)} + \tfrac{1}{2} O_{2(g)} \rightleftharpoons CO_{(g)} \qquad \Delta_r H = -111 \text{ kJ}$$

Combustion Rxns : $\Delta_c H$



Combustion rxn's are also simple to carry out in calorimeters and their Enthalpies can be combined to obtain other heats of reaction.

Consider the partial reduction of graphite to Ethylene gas. This rxn is essentially impossible to isolate without other species forming. However, The rxn Enthalpy can still be obtained via the following:

$$2\ C\ (\text{graphite}) + 2\ H_2\ (g) \longrightarrow C_2H_4\ (g) \qquad \Delta_r H^\circ_{,298} = ?$$

we can combine the following combustion Rxns:

$$2C\ (\text{graphite}) + \cancel{2\ O_2\ (g)} = 2\ CO_2\ (g) \quad ; \quad 2\Delta_c H(\text{graphite})$$

$$2\ H_2\ (g) + \cancel{O_2\ (g)} = \cancel{2H_2O}\ (g) \quad ; \quad 2\Delta_c H(H_2)$$

$$2\ CO_2\ (g) + \cancel{2H_2O\ (g)} = C_2H_4\ (g) + \cancel{3O_2}\ (g) \quad ; \quad -\Delta_c H(C_2H_4)$$

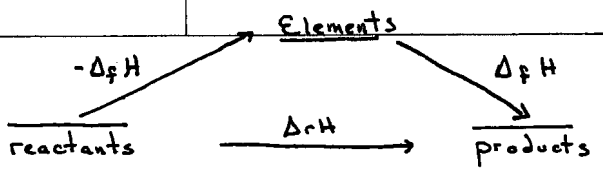
$$2\ C\ (\text{graphite}) + 2\ H_2\ (g) = C_2H_4\ (g)$$

$$\Delta_r H = 2\Delta_c H\ (\text{graphite}) + 2\Delta_c H_{(H_2)} - \Delta_c H_{(C_2H_4)}$$

$$\Delta_r H = 2(-393\ \tfrac{kJ}{mol}) + 2(-241\ kJ/mol) + (1218\ kJ/mol)$$

$$\Delta_r H = -50\ kJ/mol$$

Formation Rxns → $\Delta_f H^\circ$



Most thermochemical data is tabulated as formation reactions. The formation reaction of a substance is defined as the formation of the substance in its 'standard' state from the elements in their standard state at the Temperature of interest.

Standard State Element: Element in the form which is the most stable at $p^\ominus$ and at the Temp. under consideration. The standard state element could be a solid, liquid, or gas depending on the Temperature.

In General:

$$\Delta_r H^\circ(T) = \sum_{i=1}^{s} \nu_i \, \Delta_f H_i^\circ(T)$$

Note: by definition the Enthalpy of formation of any element in its standard state is zero!

Example: $H_2S(g) + {}^3/_2 O_2(g) \longleftrightarrow SO_2(g) + H_2O(g)$ $\quad \Delta_r H^\circ = ?$

$H_2S(g)$	=	$H_2(g) + S_{(rhombic)}$	$-\Delta_f H^\circ(H_2S)$
${}^3/_2 O_2(g)$	=	${}^3/_2 O_2(g)$	$-{}^3/_2 \Delta_f H^\circ(O_2)$
$S_{(rhombic)} + O_2(g)$	=	$SO_2(g)$	$\Delta_f H^\circ(SO_2)$
$H_2(g) + {}^1/_2 O_2(g)$	=	$H_2O(g)$	$\Delta_f H^\circ(H_2O)$
$H_2S(g) + {}^3/_2 O_2(g)$	=	$SO_2(g) + H_2O(g)$	$\Delta_r H^\circ$

$$\Delta_r H^\circ = \Delta_f H^\circ_{(SO_2)} + \Delta_f H^\circ_{(H_2O)} - \Delta_f H^\circ_{(H_2S)} - {}^3/_2 \Delta_f H^\circ_{(O_2)}$$

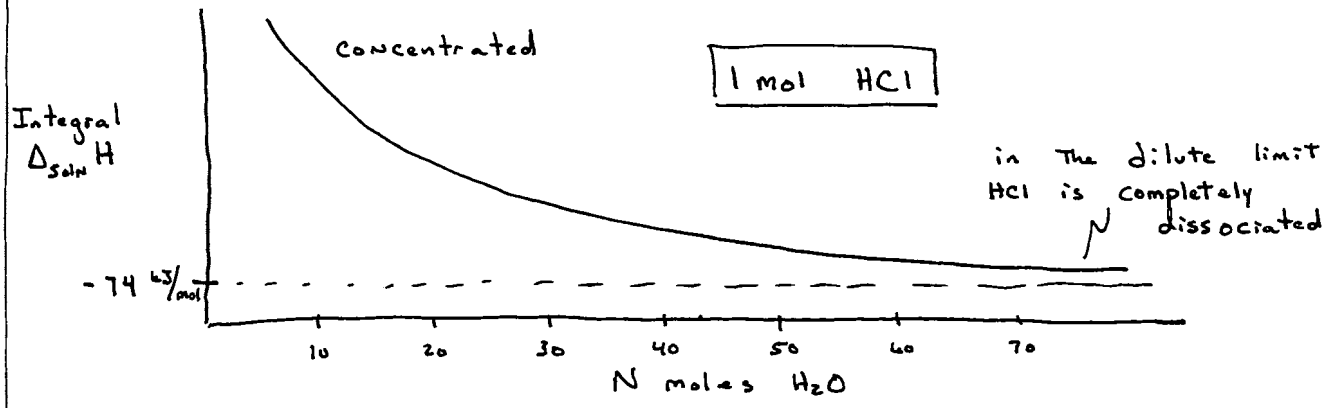
$\Delta_f H^\circ_{(O_2)} = 0$

Solution Enthalpy

When a solute is dissolved in a solvent, heat may be adsorbed or evolved. In general, the heat of solution depends on the concentration of the final solution.

The "Integral Heat of Solution" is defined as the measured Enthalpy change for the formation of a solution of 1 mol. Solute in N moles solvent.

Experimental Data:



$$HCl\ (g) \longrightarrow HCl\ (aq) \qquad \Delta H^\circ_{298} = -74\ kJ/mol$$

(aq) → completely dissociated aqueous species

Note: That the standard state of a dilute electrolyte solution is also an ideal hypothetical state — "ideal dilute state". Although the solution refers to a 1 molal soln., the Enthalpy represents that of a completely dissociated species.

Separate Enthalpies of Solution of ions cannot be measured since we always combinations of Electrolytes as charge-Neutral Substances. However, it is convenient to Tabulate Separate Solvation Enthalpies for ions using the convention:

$$\tfrac{1}{2} H_2\ (g) \longrightarrow H^+_{(aq)} + e^- \qquad \Delta_f H^\circ_{(H^+)} \equiv 0$$

$H^+_{(aq)}$ → refers to a undissociated aqueous species as written

e^- → The electron is understood to reside in an inert Electrode.

The enthalpies of formation of other ions in solution can then be readily found. (from Hess' law).

Example:

$$\tfrac{1}{2}\,Cl_2\,(g) + \tfrac{1}{2}\,H_2\,(g) \;=\; \underbrace{HCl\,(aq)}_{H^+(aq) + Cl^-(aq)} \qquad \Delta_f H^\circ = -167\ kJ$$

$$H^+(aq) + e^- \;=\; \tfrac{1}{2}\,H_2\,(g) \qquad -\Delta_f H^\circ = 0$$

$$\tfrac{1}{2}\,Cl_2\,(g) + e^- \;=\; Cl^-(aq) \qquad \Delta_f H^\circ_{(Cl)} = -167\ kJ$$

Thus:

$$\Delta_f H^\circ_{(HCl\,(aq))} = \Delta_f H^\circ_{(H^+(aq))} + \Delta_f H^\circ_{(Cl^-(aq))}$$

$\Delta_f H^\circ_{(H^+(aq))} = 0$

Temperature Dependence of $\Delta_r H$ — Kirchoff's Relation

Recall, for any reaction;

$$\Delta_r H(T,P,\underline{N}) \equiv \sum_{i=1}^{s} \nu_i \bar{H}_i(T,P,\underline{N})$$

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_{P,\underline{N}} = \sum_{i=1}^{s} \nu_i \left(\frac{\partial \bar{H}_i}{\partial T}\right)_{P,\underline{N}} = \sum_{i=1}^{c} \nu_i \bar{C}_{p,i}(T,P,\underline{N})$$

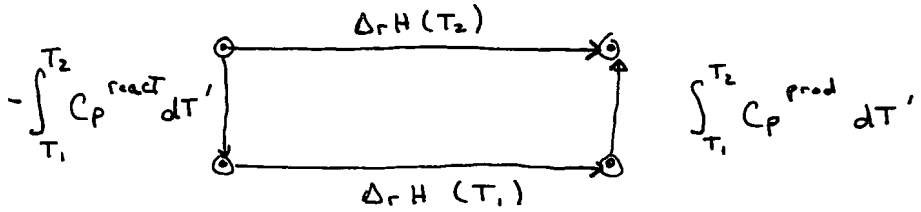
$$\boxed{\left(\frac{\partial \Delta_r H}{\partial T}\right)_{P,\underline{N}} = \Delta_r C_p}$$

Reaction Heat Capacity

where, $\Delta_r C_p \equiv \sum_{i=1}^{s} \nu_i C_{p,i}$

$$\Rightarrow \Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_p(T')\,dT'$$

This result is simply another example of Hess' Law:



$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \left(C_p^{prod} - C_p^{react.}\right) dT'$$

$$= \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_p(T')\,dT'$$

Often, heat capacity data of the reactants & products in a chemical rxn are tabulated as an analytical function of T.

$$\bar{C}_{p,i} = \alpha_i + \beta_i T + \gamma_i T^2$$

$$\Delta_r C_p = \sum_{i=1}^{s} \nu_i \bar{C}_{p,i} = \Delta_r \alpha + (\Delta_r \beta) T + (\Delta_r \gamma) T^2$$

where, $\Delta_r \alpha \equiv \sum_{i=1}^{s} \nu_i \alpha_i$

$\Delta_r \beta \equiv \sum_{i=1}^{s} \nu_i \beta_i$

$\vdots$

$$\Delta_r H^\circ(T) = \Delta_r H^\circ(298) + \int_{298}^{T} \{ \Delta_r \alpha + \Delta_r \beta T' + \Delta_r \gamma T'^2 \} dT'$$

$$= \Delta H_0^\circ + \Delta_r \alpha T + \frac{\Delta_r \beta T^2}{2} + \frac{\Delta_r \gamma T^3}{3}$$

ΔH_0° = constant ($\Delta_r H^\circ_{298}$ + integration constant)

$\Delta_r H_0^\circ$ is a constant & can be viewed as the hypothetic rxn enthalpy at 0 k. It is hypothetical since the power law expansion of $\bar{C}_{p_i}$ is not valid at low Temperatures.

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or $\bar{C}_{p_i}(T)$ data of chemical substances are sometimes Tabulated as this analytical function of T:

$$\bar{C}_{p_i}(T) = a_i + b_i T - c_i / T^2$$

Thus,

$$\Delta C^\circ_{p,rxn}(T) = \Delta a + \Delta b T - \Delta c / T^2$$

where,

$$\Delta a \equiv \sum_{i=1}^{s} \nu_i a_i$$

$$\Delta b \equiv \vdots$$

$$\vdots \quad \vdots$$

$$\Delta H^\circ_T = \Delta H^\circ_0 + \Delta a T + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{T}$$

↑ same integration constant which can be easily determined by setting T = 298k with the known value of ΔH°_{298}.