STATISTICAL MECHANICS
CH 665/PH 664
304 SB 1
T,R 2-3:50 PM

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CREDIT: 4 hours

PREREQUISITES: Graduate standing in Chemistry or Physics. **Prior courses in Quantum Mechanics, Thermodynamics and Statistics. Undergraduates must get permission from Dr. McClure before enrolling in the course.**

EXAMS: Multipart final exam only, including a take-home portion and an in class portion

HOMEWORK:
A series of homework problems will be assigned.

OFFICE HOURS: By appointment or on a 'when available' basis.

TEXT for CH 665: Statistical Mechanics by Donald McQuarrie

COURSE TOPICS in CH 665: Chapters 1 through 14 time permitting

Web Page for Solutions (more or less – mostly less): http://statmech.wikidot.com/forum:start

STATISTICAL MECHANICS PH 664
Homework Assignments*

Chapter 1, McQuarrie: Introduction and Review: pp 28-33
Do NOT turn in the following but make sure you can do them:
19, 20, 22, 23, 24, 25, 28, 29, 30, 32, 33, 41, 42, 58, 59, 61
Do turn in the following: 49, 51, 55, 56, 57.

Also do the **Thermodynamics Review Problems** handout. Only turn in the problem 6 on $S^{\ominus}(O_2, 90K)$ and make sure you compare your results to the literature values.

Chapter 2, The Canonical Ensemble: pp 47-50
Do NOT turn in the following but make sure you can do them: 5, 8, 10, 11
Do turn in the following: 14, 15, 17, and both **Ensemble Problems** handout.

Chapter 3, Other Ensembles and Fluctuations: pp 64-67
Do NOT turn in the following but make sure you can do them: 6, 8, 15
Do turn in the following: 9, 10, 20

Chapter 4, Boltzmann Statistics, FD Statistics and BE Statistics
Do NOT turn in the following but make sure you can do them: 1, 2
Do turn in the following: 18, 19, 20

Chapter 5, Ideal Monatomic Gas
Do NOT turn in the following but make sure you can do them: 1, 3, 4, 5, 9, 11
Do turn in the following: 7, 17

Chapter 6, Ideal Diatomic Gas
Do NOT turn in the following but make sure you can do them: 6, 9, 13
Do turn in the following: 20, 21, 25

Chapter 7, Classical Statistical Mechanics
Do NOT turn in the following but make sure you can do them: 1, 4, 5

Chapter 8, Ideal Polyatomic Gas
Do NOT turn in the following but make sure you can do them 3, 8, 11

Chapter 9, Chemical Equilibrium
Do NOT turn in the following but make sure you can do them: 8, 10

Chapters 10 – 14 to be assigned later.

*Assignments are subject to change depending if anyone can do the problems.

Thermodynamics Review Problems

Statistical Mechanics, PH 664

1) Compute C_P - C_V for a van der Waals gas by first deriving an expression for C_P - C_V. What must this result reduce to in the limit as $P \to 0$?

2) Defining the adiabatic compressibility as, $K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ and the isothermal compressibility as,

$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ show that $K_T = \frac{C_P}{C_V}K_S$.

3) The following identities are of great importance in thermodynamics because they permit the computation of the derivatives on the left hand sides of the expressions from the equation of state of the fluid. Derive these expressions and show they are zero for an ideal gas. There is an awkward in using b) for a van der Waals gas – what is the problem and how might you get around it, at least approximately?

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

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

4) One mole of an ideal gas is taken reversibly from the initial state $A(T_1,P_1)$ to the final state $C(T_2,P_2)$ via the two paths, ABC and AC. Calculate expressions for the work ,W and the change in V, i.e., ΔV for each
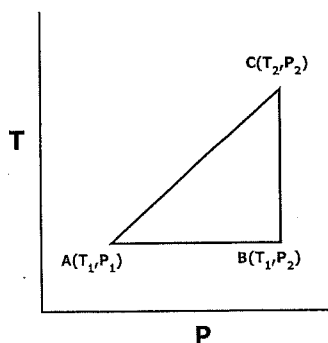

of the two paths and compare the results by filling in the following table.

	ABC	AC
ΔV		
W		

What can you conclude about path independency from your results (assuming of course that you have results and that they are correct!). Suppose you computed the cyclic integrals of dV and dW, i.e. $\oint dV$ and $\oint dW$. Are either or both zero? Which is exact and how would you prove it?

5) In the following diagram, F and I represent the Final and Initial states of a gas taken along a series of proposed paths, i.e., Gas$[P_1,V_1,T_1]$ $\longrightarrow$ Gas$[P_2,V_2,T_2]$ where $T_2 < T_1$ and $P_2 < P_1$.
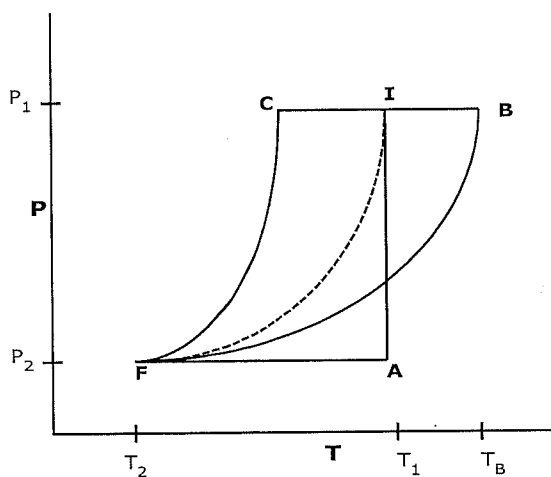
The smooth curves CF and BF represent **reversible** adiabats and the dotted curve, IF represents the actual **irreversible** adiabat, i.e., the actual process which is carried out adiabatically.

Of the many possible reversible paths linking I and F, consider the following three possibilities:

- IAF: reversible isothermal expansion followed by reversible isobaric cooling

- IBF: isobaric heating followed by a reversible adiabatic expansion to F

- ICF: isobaric cooling followed by a reversible adiabatic expansion to F

Here are the questions:

a) Begin by filling in the following table by computing expressions for each of the ΔS terms :

PATH	ΔS_{sytem}	$\Delta S_{surroundings}$	ΔS_{total}	Sign of ΔS_{sytem}
IAF				
IBF				
ICF				

b) Are all three paths **physically** possible? If not, which path(s) are not?

c) Is the point T_B unique or does there exist an arbitrary number of points on the line IB that would work just as well in order to drop a reversible adiabat to F? Prove your statement.

d) Finally, why not just drop a reversible adiabat from I to F for your model of the actual process?

e) State the Caratheodory Principle of the Second Law of Thermodynamics and discuss what relevance it has vis-à-vis this problem.

6) Calculate the absolute entropy, $S^{\circ}(90\ K)$ at 90K using the following data:

T/K	11.75	15.12	15.57	16.94	18.32	20.26	21.84	22.24	25.02	30.63	37.59	42.21	46.00	52.00	60.00	70.00	90.00
Cp/R	0.483	0.805	0.901	1.13	1.36	1.76	2.11	2.19	2.73	3.49	4.57	5.40	5.55	5.56	6.40	6.43	6.53

You will also need the following phase transition data:

$\Delta H/R(23.66\ K) = 11.28\ K$ first solid phase change

$\Delta H/R(43.75\ K) = 89.4\ K$ second solid phase change

$\Delta H/R(54.39\ K) = 53.5\ K$ fusion

See attached for the procedure. Be sure to compare your results with the literature. You may assume the gas phase is ideal.

DW McClure, Emeritus Professor of Chemistry/Physics
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2/16/2010

Thermodynamic Definitions

1. **Extensive Variable**: One that depends on the mass of the system; e.g., V, U, H, G, A, S etc. These variables are all homogeneous of degree one and additive. Mathematically, if U is extensive, $U(kn) = kU(n)$ where k is a constant.

2. **Intensive Variable**: Variable that are independent of mass; e.g., T, P, μ, etc. Homogeneous of degree zero and not additive.

3. **System**: Object of interest in which a process may or may not occur. A 'simple system' is one whose variables of state are P, V and T and in which there are no fields, inhomogenarities.

4. **Surroundings**: That region of space external to the boundaries of the system and separated from the system by 'walls' which are either' adiabatic' or 'diathermal'. The surroundings consist of two discrete parts: 1) a heat reservoir of infinite capacity that can supply or abstract heat from the system if the walls are diathermal. 2) A work source at constant pressure.

5. **Closed System**: One that cannot exchange matter with the surroundings.

6. **Open System**: One that can exchange matter with the surroundings.

7. **Isolated System**: One that is adiabatic and closed with rigid wall so no work can be done, in short, one in which there can be no interaction with the surroundings.

8. **Adiabatic Wall**: One which permits a change in the state of the system by a change in the mechanical coordinates only, i.e., through the aegis of 'work'. Alternatively, a wall that does permit the flow of heat to or from the system. Examples, dewar flask or a polystyrene cup.

9. **Adiabatic Composite**: An adiabatically enclosed structure that contains both the system and its surroundings.

10. **Diathermal Wall**: One that does permit the flow of heat e.g., a copper wall.

11. **Heat Bath or Heat Reservoir**: A portion of the surroundings that can act as an accepter or donor of heat and which remains at constant temperature due to an infinite heat capacity. The reservoir also contains a work source with an infinite capacity, i.e., the mechanical variables of the reservoir do not change over time.

12. **Thermodynamic State**: The 'state' of the system is defined once the equilibrium values of the variables P, V, T etc. have been defined which allows the equilibrium properties to be calculated.

13. **Steady State Process**: A process occurring in a non-isolated system in which the intensive variables are time invariant, i.e., T, P, μ etc. but the extensive variables like S, U, H etc. do change over time. Systems that are in steady state are NOT in equilibrium. Most industrial processes are steady state operations.

14. **Quasistatic Process**: A very slow process that is fundamentally *irreversible* but done in such a way that the system coordinates are well defined at all times. Friction may be present as well as very small concentration gradients and small temperature differences through the system. Real processes are often modeled as quasistatic processes because in real processes things actually happen over time.

15. **Equlibrium Process**: State in which none of the system coordinates (extensive or intensive) vary with time – this is not the same as steady state! In fact, nothing happens so the word 'process' is somewhat meaningless.

16. **Thermodynamic Process**: A thermodynamic process occurs when the system goes from some initial equilibrium state S_1 to a new equilibrium state S_2. The system coordinates, eg., T, P etc. will change as a result of the process. The 'path' for the process is defined by a specification of the equation of state.

17. **Isothermal Process**: One carried out a constant temperature – generally the system wall would be diathermal so that heat transfer could occur but in the case of an adiabatic wall, electrical work could be done to add but not remove energy and so we have an example of a Carathe'odory inaccessible state.

18. **Adiabatic Process**: One without heat transfer between the system and surroundings, i.e., $dQ = 0$ over the course of the process.

19. **Reversible Process**: An infinitely slow process that can be reversed at any time in such a way as to restore BOTH the system and surrounding to their previous states. For a process to be reversible there must be no friction or finite temperature, pressure or concentration differences anywhere in the system. A reversible process is an equilibrium process in which nothing ever happens, and the use of reversibility as a model for a real process is often wildly optimistic.

20. **Equation of State**: An equation of the form $F(x_1, x_2, ...) = 0$ where $x_1, x_2....$ are the system variables or coordinates whose specification define the equilibrium state of the system, e.g., $PV - RT = 0$ defines the variables that specify the equilibrium state of an ideal gas.

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Math Background

Partial Differentiation

Consider the function

$$z = f(x, y)$$

OR $\quad F(x, y, z) = \emptyset$
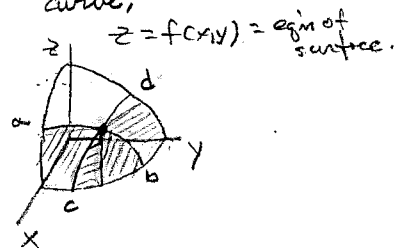
which describes a 3 space surface

Query - How does a point on the surface move under the following conditions:

a) x varies; y constant, ie what is $\left[\dfrac{\partial z(x)}{\partial x}\right]_y$ const y (slope cd)

b) y " ; x " , " " " $\left[\dfrac{\partial z(y)}{\partial y}\right]_x$ " x (slope ab)

The /// curve results from an intersection of the plane x=const & the surface & ≡ curve is for the y=const plane intersecting the curve,

$z = f(x,y) = $ eqn of surface.

Cases a & b

Partial Differentiation:
Example:

$$z = f(x, y) = x^2 y + y^2 + 3$$

$$\left(\frac{\partial z}{\partial x}\right)_y \equiv \left(\frac{\partial f}{\partial x}\right)_y \equiv f_x = 2xy$$

$$\left(\frac{\partial z}{\partial y}\right)_x \equiv \left(\frac{\partial f}{\partial y}\right)_x \equiv f_y = x^2 + 2y$$

Note: Formally, for $z = f(x,y)$

$$\left(\frac{\partial f}{\partial x}\right)_y = \lim_{\Delta x \to 0} \frac{f(x+\Delta x, y) - f(x,y)}{\Delta x}\Bigg|_{y\,con.}$$

where the point resides on a curve generated by the intersection of a plane parallel to the x & z axes and the curve $z = f(x,y)$

Note:

$$\left(\frac{\partial z}{\partial x}\right)_x = \left(\frac{\partial z}{\partial x}\right)_z = 0$$

Ie, cannot hold a variable constant & differentiate WRT to it.

furthermore one may ^again diff. WRT a new variable:

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x \equiv \frac{\partial}{\partial y} f_x \equiv f_{yx} = \left[\frac{\partial}{\partial y}(2xy)\right]_x = 2x$$

Read right to left WRT order

and

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y \equiv \frac{\partial}{\partial x} f_y \equiv f_{xy} = \left[\frac{\partial}{\partial x}(x^2+2y)\right]_y = 2x$$

ie,

$$\boxed{f_{yx} = f_{xy}}$$

which is generally true for mixed partials provided $f(x,y)$ and its derivatives are continuous. Always true in Thermo. applications. Thus, usually the order of diff. is material.

Case c

Total Differentials:

Here both x & y vary simultaneously so

$$z = f(x,y)$$

$$dz \equiv df(x,y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$= f_x\, dx + f_y\, dy$$

} either notation

If $z = f(x_1, x_2, \cdots x_n)$ then

$$dz = \sum_{i=1}^{n} \left(\frac{\partial z}{\partial x_i}\right)_{x_j \neq i} dx_i \qquad \text{all } j \neq i \qquad \text{for } n \text{ variables.}$$

Example: $z = f(x,y) = x^2 y + xy + y$; $f_x = \left(\frac{\partial f}{\partial x}\right)_y = 2xy + y$; $f_y = x^2 + x$

so $dz = f_x\, dx + f_y\, dy = (2xy + y)\, dx + (x^2 + x + 1)\, dy$

Useful Relations:

Consider a fn. $z = f(x,y)$, Then

a) $\left(\dfrac{\partial y}{\partial x}\right)_z \left(\dfrac{\partial x}{\partial z}\right)_y \left(\dfrac{\partial z}{\partial y}\right)_x = -1$

b) $\left(\dfrac{\partial y}{\partial x}\right)_z \left(\dfrac{\partial x}{\partial y}\right)_z = 1$ OR $\left(\dfrac{\partial y}{\partial x}\right)_z = \dfrac{1}{\left(\dfrac{\partial x}{\partial y}\right)_z}$

c) $\left(\dfrac{\partial y}{\partial T}\right)_z \left(\dfrac{\partial T}{\partial x}\right)_z = \left(\dfrac{\partial y}{\partial x}\right)_z$

Implicit Functions:

An implicit function is written (in 2 dimensions for example)

$$f(x,y) = 0$$

Suppose we wish to calculate dy/dx. Usual procedure is to solve for y & differentiate. Instead we write

$$df(x,y) = \left(\dfrac{\partial f}{\partial x}\right)dx + \left(\dfrac{\partial f}{\partial y}\right)dy = f_x\,dx + f_y\,dy = 0$$

OR

$$\dfrac{dy}{dx} = -\dfrac{f_x}{f_y}$$

Example

Calc. dy/dx for $y e^x + \cos y = 0$, Can't solve for y but the formula gives

$$y' = -\dfrac{y e^x}{e^x - \sin y}$$

Applications

1) Suppose we wish to evaluate $\left(\frac{\partial V}{\partial P}\right)_T$ for a VW gas

$$\left(P + \frac{a}{v^2}\right)(V - b) = RT$$

solving for $V = V(P,T)$ would require solving a cubic.⊛ Two methods:

$$\begin{cases} ⊛ \text{ Ie,} \\ PV^3 - V^2(Pb + RT) + av - ab = 0 \end{cases}$$

a) $\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = -1$ so

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P} = -\frac{\left(\frac{\partial T}{\partial P}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_P}$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{V - b}{R}$$

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{R}\left[P - \frac{a}{V^2} + \frac{2ab}{V^3}\right]$$

so

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{(V-b)}{\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)}$$

b) Alternativey we have

$$\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial V}\right)_T = 1 \quad \text{so}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\left(\frac{\partial P}{\partial V}\right)_T} \quad \text{so from } P = -\frac{a}{V^2} + \frac{RT}{V - b}$$

we can calc $(\partial P/\partial V)_T$ as before.

2) Given that $H = U + PV$ & that $U = U(T,V)$ show that

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

Step 1 - Calculate dH

$dH = dU + PdV + VdP$ $\underline{OR}$ since $H = H(U,P,V)$ then

$$dH = \left(\frac{\partial H}{\partial U}\right)_{P,V} dU + \left(\frac{\partial H}{\partial P}\right)_{U,V} dP + \left(\frac{\partial H}{\partial V}\right)_{U,P} dV$$

but $\left(\frac{\partial H}{\partial U}\right)_{P,V} = 1$; $\left(\frac{\partial H}{\partial P}\right)_{U,V} = V$; $\left(\frac{\partial H}{\partial V}\right)_{U,P} = P$

Also:

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

So

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

Step 2

Divide thru by dT & restrict to const. P

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

OR, at const P

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

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

At this point, our equation cannot be used, but we shall soon derive a relationship between $\left(\frac{\partial U}{\partial V}\right)_T$ & P, V & T which will make the expression useful.

Linear Differential Forms (LDF's) or Pfaffians

A LDF is a simple linear differential equation of the form:

$$L(x_1, x_2, \ldots) = \bar{X}_1(x_1, x_2 \ldots) dx_1 + \bar{X}_2(x_1, x_4, \ldots) dx_2 + \cdots$$

or, in two dimensions,

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

Example:

$$L(x,y) = 2xy \, dx + x^2 dy \quad \text{where} \quad M = 2xy \text{ \& } N = x^2$$

Classification of LDF's

Two flavors:

a) Exact: Defn. If, given a LDF $L(x,y)$ there exists a function $f(x,y)$ s.t. $df = L$ then we say $L(x,y)$ is exact.

Example: Is $L(x,y) = 2xy \, dx + x^2 dy$ exact?
Ans: Yes because if $f(x,y) = x^2 y$ then

$$df(x,y) \overset{\text{always}}{\underset{\text{True}}{=}} f_x dx + f_y dy \overset{\text{True}}{\underset{\substack{\text{only if} \\ \text{exact}}}{=}} 2xy \, dy + x^2 dy \equiv L(x,y)$$

and

$$\left(\frac{\partial f}{\partial x}\right)_y = 2xy = M(x,y) \; ; \; \left(\frac{\partial f}{\partial y}\right)_x = x^2 = N(x,y)$$

b) Inexact: Defn. Not exact

Example: $L(x,y) = xy \, dx + x^2 dy$
There is no function $f(x,y)$ s.t. $df = L(x,y)$.

Criterion for Exactness

Given an exact LDF $L(x,y) = M(x,y)dx + N(x,y)dy$
we have the equality $df(x,y) = L(x,y)$ so we can write

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = M(x,y)dx + N(x,y)dy$$

so
$$\left.\begin{array}{c} \left(\dfrac{\partial f}{\partial x}\right)_y = M(x,y) \\[2em] \left(\dfrac{\partial f}{\partial y}\right)_x = N(x,y) \end{array}\right\} \text{True since } L(x,y) \text{ is exact}$$

Then provided all derivatives are continuous
we have, since $f_{yx} = f_{xy}$, that is,

$$\left[\frac{\partial}{\partial y}\left(\underbrace{\frac{\partial f}{\partial x}}_{M(x,y)}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\underbrace{\frac{\partial f}{\partial y}}_{N(x,y)}\right)_x\right]_y \quad \text{always true}$$

OR, subst,
$M \& N$ for $f_x \& f_y$
$$\left[\frac{\partial M(x,y)}{\partial y}\right]_x = \left[\frac{\partial N(x,y)}{\partial x}\right]_y \quad \text{True if exact}$$

Thus a necessary condition that $L(x,y)$ be
exact is that, for a LDF $L(x,y) = M(x,y)dx + N(x,y)dy$

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

Can also show this sufficient as well.
Example: $L(x,y) = 2xy\,dx + x^2\,dy$ is exact since
$$\frac{\partial}{\partial y}(2xy) = \frac{\partial}{\partial x}(x^2) = 2x \quad \& \quad f(x,y) = x^2 y$$

Comment

In terms of vectors we have, say

$$dW = \bar{F} \cdot d\bar{R} = F_x\, dx + F_y\, dy + F_z\, dz$$

where $\bar{F} \cdot d\bar{R}$ is usually _inexact_.

The criterion for exactness in terms of vectors is then

$$Curl\ \bar{F} = \bar{0}$$

provided the field is simply connected. That is,

$$Curl\ \bar{F} = \bar{\nabla} \times \bar{F} = \begin{vmatrix} i & j & k \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ F_x & F_y & F_z \end{vmatrix} = \bar{0}$$

OR
$$\frac{\partial F_x}{\partial y} = \frac{\partial F_y}{\partial x}, \quad \frac{\partial F_y}{\partial z} = \frac{\partial F_z}{\partial y}, \quad \frac{\partial F_x}{\partial z} = \frac{\partial F_z}{\partial x}.$$

If $curl\ \bar{F} \neq \bar{0}$ then the field is _not_ conservative, $\int dW$ is path dependent and friction is usually present.

LINE INTEGRALS

An LDF is a linear diff. eq'n & its integral is called a line Integral. In particular:

1) Line integrals are not areas or lengths.

2) Line integrals reduce to the usual kind of integral if the path is parallel to a coordinate axis. Thus

$$\int_C [M(x,y)\,dx + N(x,y)\,dy] = \int M\,dx \quad \text{if } C = y = \text{const.}$$

Properties of Line Integrals of EXACT Differentials.

1) The line integral of an exact LDF is path independent.
   Proof: If $L(x,y)$ is exact, $\exists$ a $f(x,y)$ s.t. $df = L$,

   so $\int_C L(x,y) = \int_a^b (M\,dx + N\,dy) = \int_a^b df = f(b) - f(a)$
   where a, b denote x_1, y_1 & x_2, y_2

2) The cyclic line integral of an exact LDF is zero.
   Proof: In proof 1, $a \equiv b$ so that

   $$\oint L(x,y) = \oint (M\,dx + N\,dy) = f(b) - f(a) = 0 \quad \text{as } a \equiv b.$$

Summary

If $L(x,y)$ is exact, then

a) $\exists$ an $f(x,y)$ s.t. $df = L(x,y)$

b) $\oint_C df = 0$ and $\int_a^b df = f(b) - f(a)$ for all C in the domain
   i.e. $\int_a^b df$ is indep. of path.

c) $\left(\dfrac{\partial M}{\partial y}\right)_x = \left(\dfrac{\partial N}{\partial x}\right)_y$ — Usual exactness test

Comment: All thermodynamic functions except dQ & dw are expressed as exact LDF's with the properties of a–c above

Example Using The Reciprocity Condition (# 9.1)

Given That $du = Tds - Pdv$ & $dA = -Pdv - SdT$, show that

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$$

From $du = Tds - Pdv$ we have

$$\frac{du}{dv} = T\frac{ds}{dv} - P\frac{dv}{dv}$$

OR

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P$$

What is:
$$\left(\frac{\partial u}{\partial P}\right)_T ?$$
Need $dG = -SdT + vdP$

Show both
$$\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial u}{\partial P}\right)_T = \phi$$
for an IG

From $dA = -Pdv - SdT$ & The fact that dA is exact, we have

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad \text{so we have}$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P \quad QED$$

See

We can now redo our previous example, PA7, where we found

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial u}{\partial T}\right)_v + \left[P + \left(\frac{\partial u}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial T}\right)_P$$

which, on substitution gives

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial u}{\partial T}\right)_v + \left[P + T\left(\frac{\partial P}{\partial T}\right)_v - P\right]\left(\frac{\partial v}{\partial T}\right)_P$$

$$= \left(\frac{\partial u}{\partial T}\right)_v + T\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_P$$

But $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$ & $C_v \equiv \left(\frac{\partial u}{\partial T}\right)_v$ so

$$C_P = C_v + T\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_P$$

$$= C_v + nR \text{ for an I.G.}$$

Legendre Transforms

It is useful to have a method to change variables in a differential form. Suppose we have the EXACT LDF

$$d\underline{Z}(x,y) = \underline{X}(x,y)\,dx + \underline{Y}(x,y)\,dy \quad \text{where}$$

$$\underline{X}(x,y) = \left(\frac{\partial \underline{Z}}{\partial x}\right)_y$$

$$\underline{Y}(x,y) = \left(\frac{\partial \underline{Z}}{\partial y}\right)_x$$

Now suppose we want the new function

$$dR(\underline{X},\underline{Y}) = x\,d\underline{X}(x,y) + y\,d\underline{Y}(x,y) \quad \text{change } X \text{ \& } Y.$$

Procedure :

Change of one variable first:

$$R(\underline{X},\underline{Y}) = \underline{Z}(x,y) - x\,\underline{X}(x,y)$$

$$dR = d\underline{Z} - x\,d\underline{X} - \underline{X}\,dx$$

Substitution for $d\underline{Z}$ above gives

$$dR(\underline{X},\underline{Y}) = \underline{X}\,\cancel{dx} + \underline{Y}\,dy - x\,d\underline{X} - \underline{X}\,\cancel{dx}$$

$$= \underline{Y}\,dy - x\,d\underline{X} \quad \text{ie} \quad \underline{X}\,dx \rightarrow x\,d\underline{X}$$

Likewise, for $R(\underline{X},\underline{Y}) \equiv \underline{Z} - x\underline{X} - y\underline{Y}$ we have

$$dR = -x\,d\underline{X} - y\,d\underline{Y} \quad \text{or}$$

$$\left.\begin{array}{l} \underline{X}\,dx \rightarrow -x\,d\underline{X} \\ \underline{Y}\,dy \rightarrow -y\,d\underline{Y} \end{array}\right\} \quad \text{ie both variables transformed with a change in sign}$$

The importance of this method lies in the fact that you can change variable without losing information.

Application

Starting <u>w</u> the Gibbs fundamental eq'n in the energy or entropy representations, we can derive the other potentials, eg,

$$dU = Tds - pdv + \sum \mu_i dn_i \quad \text{energy representation}$$

You can use the Legendre transform to get:

Differential Expression	New Function	Transform
$dH = Tds + Vdp + \sum \mu_i dn_i$	$H = U + PV$	$-pdv \rightarrow Vdp$
$dA = -SdT - pdv + \sum \mu_i dn_i$	$A = U - TS$	$Tds \rightarrow -SdT$
$dG = -SdT + Vdp + \sum \mu_i dn_i$	$G = U + PV - TS$ $= H - TS$	$\begin{cases} -pdv \rightarrow Vdp \\ -Tds \rightarrow SdT \end{cases}$
$d\Phi_1 = -Ud(\frac{1}{T}) + \frac{P}{T}dv + \sum \frac{\mu_i}{T} dn_i$	$\Omega = U - TS - \sum \mu n$ massieu function	
$d\phi_2 = -Ud(\frac{1}{T}) - Vd(\frac{P}{T}) + \sum \frac{\mu_i}{T} dn_i$ Planck "		
$d\Omega = -SdT - pdv - \sum n_i d\mu_i$ Grand Potential		

These 'potentials' or 'state functions' are all exact LDE's and can be integrated w.r.t. mass,

INTEGRATION OF THE POTENTIALS WRT M H?

Two Methods:

a) Euler's Theorem

See any Thermodyamics text

b) Direct Integration constant Intensive Variables

Example:

$$dU = Tds - pdv + \sum \mu_i dn_i$$

S, V, n_i etc. are all extensive variables with the property that, $S(\kappa n) = \kappa S(n)$ etc.

So we can write

$$du = Tds - pdv + \sum \mu_i dn_i$$

$$\int_n^{kn} du = T \int_n^{kn} ds - p \int_n^{kn} dv + \sum_i \int_n^{kn} \mu_i dn_i$$

$$u(kn) - u(n) = T[S(kn) - S(n)] - p[V(kn) - V(n)] + \sum_i \mu_i [$$

$$k u(n) - u(n) = T[kS(n) - S(n)] - \cdots \text{etc}.$$

$$u(n)[k-1] = TS(n)[k-1] - \cdots - \text{OR}$$

dividing out the k-1 factor & dropping the n,

$$u = TS - pv + \sum_i \mu_i n_i$$

Likewise:

$$G = \sum_i \mu_i n_i \quad \text{since} \quad dT = dp = \phi$$

Remember: Only the <u>extensive</u> variables contribute to the result.

See the Table on the next page.

Gibbs - Duhem Equations

From the table on the next page we have:

① $du = Tds - pdv + \sum \mu dn$ which, on integration gives

② $u = TS - pv + \sum \mu n$ then diff. u & comparing with

eqn 1 gives

From 2: $du_2 = Tds + sdT - pdv - vdp + \sum \mu dn + \sum n d\mu$

" 1: $du_1 = Tds - pdv + \sum \mu dn$ or on equating

we get the Gibbs Duhem eq'n, ie,

$$sdT - vdp + \sum n_i d\mu_i = 0 \quad \text{or at const } T, p \text{ we have}$$

$$\sum \mu_i dn_i = \phi$$

TABLE OF THERMODYNAMIC POTENTIALS, THEIR INTEGRATED FORMS, TRANSFORM EQUATIONS AND THE CHARACTERISTIC FUNCTIONS

Differential Forms	Transforms to dU	Integrated Form	Characteristic Function	Fixed Variables/Fluctuations
Gibbs Fundamental Equation In the Energy Representation $$dU = TdS - PdV + \sum_i \mu_i dn_i$$		$$U = TS - PV + \sum_i \mu_i n_i$$		
Gibbs Fundamental Equation in the Entropy Representation $$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T}\sum_i \mu_i dn_i$$		$$S = \frac{U}{T} + \frac{PV}{T} - \frac{1}{T}\sum_i \mu_i n_i$$	Microcanonical Ensemble $$S = k\log\Omega(N,V,E)$$	N,V,E Fixed No Fluctuations
$$dH = TdS + VdP + \sum_i \mu_i dn_i$$	$H = U + PV$ $-PdV \to VdP$	$$H = TS + \sum_i \mu_i n_i$$		
$$dA = -SdT - PdV + \sum_i \mu_i dn_i$$	$A = U - TS$ $TdS \to -SdT$	$$A = -PV + \sum_i \mu_i n_i$$	Canonical Ensemble $$A = -kT\log Q(N,V,T)$$	N,V,T Fixed Fluctuations in E, P
$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$	$G = U + PV - TS$ $-PdV \to VdP$ $TdS \to -SdT$	$$G = \sum_i \mu_i n_i$$	Isobaric, Isothermal Ensemble $$G = -kT\log\Delta(N,T,P)$$	N,T,P Fixed Fluctuations in E, V
Massieu Function $$d\Phi_1 = -Ud(\tfrac{1}{T}) + (\tfrac{P}{T})dV - \frac{1}{T}\sum_i \mu_i dn_i$$	Use the Entropy Representation	$$\Phi_1 = \frac{PV}{T} - \frac{1}{T}\sum_i \mu_i n_i = -\frac{A}{T}$$		
Planck Function $$d\Phi_2 = -Ud(\tfrac{1}{T}) - Vd(\tfrac{P}{T}) - \frac{1}{T}\sum_i \mu_i dn_i$$	Use the Entropy Representation	$$\Phi_2 = -\frac{1}{T}\sum_i \mu_i n_i = -\frac{G}{T}$$		
Grand Potential Function $$d\Omega = -SdT - PdV - \sum_i n_i d\mu_i$$	$\Omega = U - TS - \sum \mu n$ $TdS \to -SdT$ $\sum \mu dn \to -\sum n d\mu$	$$\Omega = -PV$$	Grand Canonical Ensemble $$\Omega = -kT\log\Xi(V,T,\mu)$$	V,T,μ Fixed Fluctuations in E, N

3-30-2010

Application of The Gibbs Dunem Eq'n

Binary Solutions

Assuming both phases are volatile (eg. acetone $+ H_2O$)
Then we can differentiate between ideal solutions
for which The solvent obeys Raoults Law where

$$P_1 = P_1^{\ominus} X_1 \qquad 1 \equiv \text{solvent}, \ P^{\ominus} = \text{v.i.p. pure component}$$

over The entire composition range, ie $0 \leq X_1 \leq 1$. The
GD eq'n can be used to show The solute must
also obey R.L., io $P_2 = P_2^{\ominus} X_2 \quad 0 \leq X_2 \leq 1$.

For Non-ideal solutions however, There will always
be a region over which The solvent obeys R.L.,
in particular when $\underset{X_1 \to 1}{\text{Limit}} \ P_1 \to P_1^{\ominus} X_1$. However
in This region The solute does not obey R.L. but
instead obeys Henry's law, io $P_2 \to k X_2, \ X_2 \to \emptyset$.
This follows from The G-D equation:

$$n_1 d\mu_1 + n_2 d\mu_2 \to X_1 d\mu_1 + X_2 d\mu_2 \text{ on dividing by}$$

$n_T = n_1 + n_2$. Here $X_1 + X_2 = 1$. Furthermore

$$\mu_i(T,P) = \mu_i^{\ominus}(T) + RT \log \frac{f_i}{f^{\ominus}} \approx \mu_i^{\ominus}(T) + RT \log \frac{P_j}{P^{\ominus}}$$

$$= \mu^{\ominus}(T) + RT \log P_i \quad \text{as } P^{\ominus} \overset{\Delta}{=} 1 \text{ bar}, \quad i = 1,2$$

Then, since $\mu_j = \mu_j(X_j)_{T,P}$ so

$$d\mu_j = RT \left(\frac{\partial \log P_j}{\partial x_j} \right)_{T,P} dX_j \quad j = 1,2$$

Substitution into The G-D eqin gives:

$$X_1 \left(\frac{\partial \log P_1}{\partial X_1}\right)_{T,P} dX_1 + X_2 \left(\frac{\partial \log P_2}{\partial X_2}\right)_{T,P} dX_2 = \emptyset$$

OR, since $X_1 + X_2 = 1$ & $dX_1 = -dX_2$ we have

$$X_1 \left(\frac{\partial \log P_1}{\partial X_1}\right)_{T,P} = X_2 \left(\frac{\partial \log P_2}{\partial X_2}\right)_{T,P} \quad \text{another form of the GD eq'n}$$

Now when The solvent obey R.L. we have

$$P_1 \to X_1 P_1^{\dagger} \text{ as } X_1 \to 1, X_2 \to \emptyset \text{ so}$$

$$X_1 \left(\frac{\partial \log P_1}{\partial X_1}\right)_{T,P} \to 1 \implies X_2 \left(\frac{\partial \log P_2}{\partial X_2}\right)_{T,P} = 1$$

And which on integration over The region for which R.L. holds, gives:

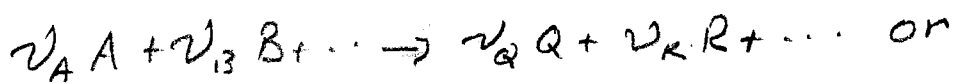$$\log P_2 = \log X_2 + \text{const} \quad \text{. OR}$$

$$P_2 = e^{\text{const}} \cdot X_2 \quad \text{where } e^{\text{const}} \neq P_2^{\dagger} \text{ as in RL.}$$

Define $K_{H,2} = e^{\text{const}}$ and call it Henry's const

Thus if The solvent obeys R.L. over The range from X_1' to 1 Then The solute obeys RL from $X_2 = 1 - X_1'$ to $X_2 = \emptyset$.

Chemical Reactions

Consider an arb. chemical reaction:

$$\nu_A A + \nu_B B + \cdots \rightarrow \nu_Q Q + \nu_R R + \cdots \quad \text{or}$$

$$\sum_i \nu_i \underline{X}_i = \phi \quad \text{where} \quad \begin{cases} \nu_{Reactants} < \phi \\ \nu_{products} > \phi \end{cases}$$

And, at const. T & P, since

$$dG = -SdT + Vdp + \sum \mu_i dn_i$$

we have

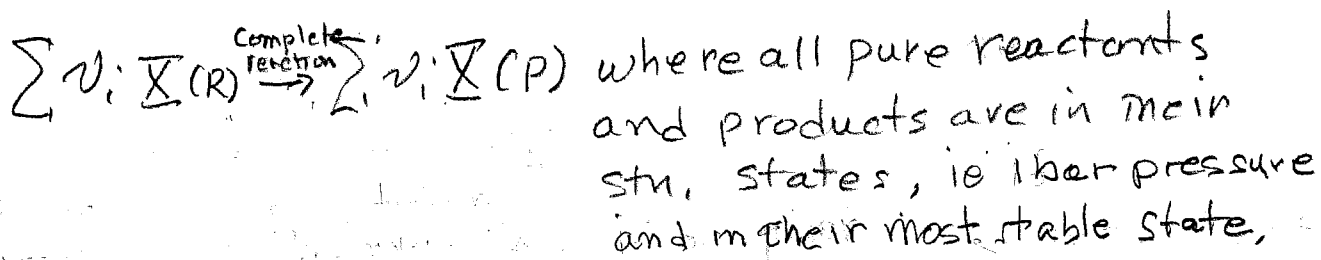$$\Delta G_{T,P} = \sum_i \mu_i n_i \equiv \sum_i \mu_i \nu_i$$

OR

$$\Delta G_{T,P} = \sum_i \nu_i \left[\mu_i^\ominus + RT \log a_i \right]$$

$$= \sum_i \nu_i \mu_i^\ominus + RT \sum_i \nu_i \log a_i$$

and,

$$\Delta G_{T,P}^\ominus \equiv \sum_i \nu_i \mu_{i(T)}^\ominus = \sum_i \nu_i \Delta G_{i,f}^\ominus$$

where $\Delta G_{T,P}^\ominus$ is the stn. Gibbs energy of reaction for the 'stn. state reaction', defined as:

$$\sum_i \nu_i \underline{X}(R) \xrightarrow[\text{reaction}]{\text{complete}} \sum_i \nu_i \underline{X}(P)$$ where all pure reactants and products are in their stn. states, ie 1 bar pressure and in their most stable state,

$\Delta G_{i,f}^\ominus$ is tabulated in most thermo. texts. Note that $\Delta G_{i,f}^\ominus$ & $\Delta H_{i,f}^\ominus \equiv \phi$ for the pure elements in their stn. states & usually at 1 bar press., most stable form etc.
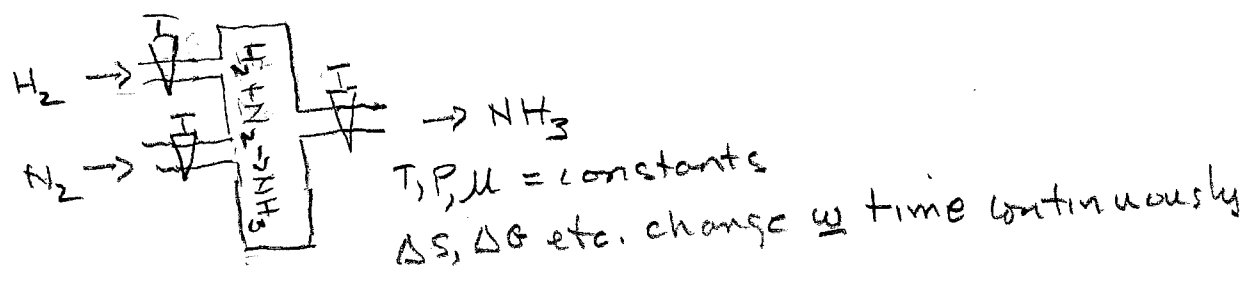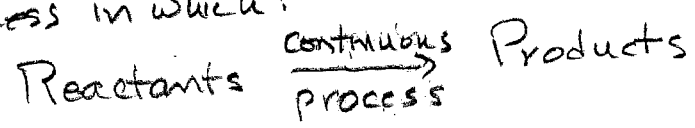
We now write:

$$\Delta G_{T,P} = \Delta G_{T,P}^{\ominus} + RT \sum \nu_i \log a_i = \Delta G_{T,P}^{\ominus} + RT \log \left[\prod a_i^{\nu_i} \right]$$

Define $J \equiv \prod a_i^{\nu_i}$ so

$$\Delta G_{T,P} = \Delta G_{T,P}^{\ominus} + RT \log J \quad \text{where}$$

$$J = \prod a_i^{\nu_i} = \frac{\prod a_i^{\nu_i} (Prod)}{\prod_i a_i^{\nu_i} (Reod's)} \qquad \text{all } \nu_i > 0$$

Here J refers to a steady state process, <u>not equlib.</u> in which the intensive variables are fixed w time but not the extensive variables, ie J represent the steady state process in which:

$$\text{Reactants} \xrightarrow[\text{process}]{\text{continuous}} \text{Products}$$

$$\to NH_3$$
$$T, P, \mu = \text{constants}$$
$$\Delta S, \Delta G \text{ etc. change } \underline{w} \text{ time continuously}$$

Equilibrium

At equilibrium $\Delta G_{T,P} = \phi$ so

$$\Delta G_{T,P} = \sum \nu_i \mu_i = \Delta G_{T,P}^{\ominus} + RT \log J_{eq} = \phi \quad \text{or,}$$

a) $\sum' \nu_i \mu_i = \phi$ const T, P general condition for reaction equilibrium

b) Define $J_{eq} \equiv K$ in which case

$$\Delta G_{T,P}^{\ominus} = -RT \log K^{\ominus}$$

Note that we can get $\Delta G_{T,P}^{\ominus}$ by meas. $K^{\ominus}$ & conversely, get $K^{\ominus}$ from tables of $\Delta G_f^{\ominus}(T,P)$ for the stn. state reaction.

where the equilib. constant K^θ is given by:

$$K^\theta = \prod_i a_i^{\nu_i} \text{(equlib)} \quad vs \quad J = \prod a_i^{\nu_i} \text{(s.s.)}$$

So finally, we have the general expression

$$\Delta G_{T,P} = RT \log \frac{J}{K^\theta} = \sum_i \nu_i \mu_i$$

Driving Force for Reactions

a) $\Delta G_{T,P} > 0 \Rightarrow \sum_i \nu_i \mu_i (P) > \sum_i \nu_i \mu_i (R)$ or $J > K$ and the reaction cannot proceed left to right.

b) $\Delta G_{T,P} < 0 \Rightarrow \sum_i \nu_i \mu_i (R) > \sum_i \nu_i \mu_i (P)$ or $J < K$ so the may proceed as written

c) $\Delta G_{T,P} = \phi \Rightarrow \sum_i \nu_i \mu_i (R) = \sum_i \nu_i \mu_i (P)$ or $J = K$ ie, we have equilib.

Temp. Dependence for ΔG^θ

We have

$$\Delta G = \Delta H - \Delta(TS) = \Delta H - T\Delta S \quad const. T$$

But $dG = -s\,dT + v\,dp$ so

$$-s = \left(\frac{\partial G}{\partial T}\right)_P \quad or \quad \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \quad so$$

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \quad OR$$

$$\left[\frac{\partial \Delta G/T}{\partial T}\right]_P = -\frac{\Delta H}{T} \quad \text{which reads for } \Delta G^\theta = -RT\log K^\theta_{(T)}$$

$$\left[\frac{\partial \log K^\theta_{(T)}}{\partial T}\right]_P = \frac{\Delta H_R^\theta}{RT^2}$$

and where,

$$\Delta H_R^{\ominus}(T) = \sum_i \nu_i \Delta H_{fi}^{\ominus}(T) \quad OR$$

$$\log K^{\ominus}(T_2) = \log K^{\ominus}(T_1) + \int_{T_1}^{T_2} \left\{ \Delta H_R^{\ominus}(T)/RT^2 \right\} dT$$

where

$$\Delta H_R^{\ominus}(T) = \Delta H_R^{\ominus}(T_0) + \int_{T_0}^{T} \sum_i \nu_i C_{P,i}^{\ominus}(T) \, dT$$

$$C_{P,i} = a_0 + a_1 T + a_2 T^2 \quad \text{or} \quad a_0 + a_1 T + \frac{a_2'}{T^2} \quad \text{etc.}$$

See problem 1-33 p 29.

Third Law Computations

Expressions for ΔS^α for Simple Systems, System Only

$$dS^\alpha = \frac{C_V \, dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$dS^\alpha = \frac{C_P \, dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

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

$$\Delta S^\alpha = \frac{\Delta_{\sigma_1}^{\sigma_2} H_{Trans}}{T_{Trans}} \quad \text{phase transitions from phase } \sigma_1 \text{ to phase } \sigma_2$$

Make sure you know how to derive these relationships.

For more on ΔS calculations from the 2nd Law see paper: Calculation of Entropy for Arbitrary Processes on the web page under Lecture Documents!

CALCULATION OF THE ENTROPY FOR AN ARBITRARY PROCESS

By definition, the entropy S is defined in terms of _reversible processes_ only, whereas real processes are always irreversible; so the question is, how do we calculate the entropy of an arbitrary irreversible process?

In the following diagram, we imagine an adiabatically isolated 'composite' which contains within it the **surroundings β**, and the **system α**, which is separated from β by an adiabatic or diathermal wall. The surroundings, β of the composite are composed of work and heat reservoirs of an infinite extent and at constant volume so that the properties of the surroundings (eg, the temperature) do not change when β interacts with α. The surroundings, β, are sometimes called the 'universe' but we don't need anything that grandiose – in fact, the surroundings are often nothing more than a simple constant temperature bath containing the system which itself may be a glass vessel containing a reaction mixture. The glass is then the diathermal wall separating α and β. The constant temperature bath might or might not be adiabatically shielded.

adiabatic wall

Work and Heat Reservoirs

α   β

Adiabatic or diathermal wall
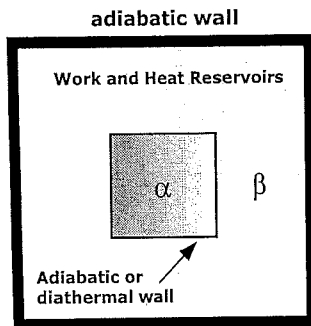
Second Law

Using our imagined concept of an adiabatically isolated 'composite', we can write,

$dS_{total} = dS_{sys} + dS_{surr} \equiv dS^{\alpha} + dS^{\beta}$ for the composite

The second law then states:

If a process occurs in an 'isolated composite', then

$$dS_{total} \geq 0 \quad where \begin{cases} > \text{ implies a spontaneous irreversible process} \\ = \text{ implies a reversible process, i.e., equilbrium} \\ < 0 \text{ implies an impossible process} \end{cases}$$

Thus dS_{total} can serve as a general criterion for irreversible change. Note that dS_{sys} and dS_{surr} can have any sign as long as the total is positive. The only problem is that in order to use dS_{total} as a criterion for say, determining if an arbitrary reaction can actually occur spontaneously is that dS_{surr} is generally difficult or often impossible to calculate. That is why we preferably use $dG_{T,P}$ or $dA_{T,P}$ for this purpose since all of the terms in these functions refer to the system only, and not the surroundings. The price we pay for this convenience however is the loss of generality because of the restrictions of constant T, P or V.

This then brings us to the question of just how we actually calculate ΔS^{α} and ΔS^{β} in order to get ΔS_{total}. We start with the system entropy.

System Entropy Change

Here we devise a **reversible** analog or model of the actual process which connects the final and initial states of the system. Since dS is exact then dS (reversible model) = dS (actual process). Note that the reversible model need not have anything in common with the actual process except the same initial and final states!

We then compute $\Delta S^{\alpha} = \int \dfrac{dQ_{rev}^{\alpha}}{T^{\alpha}}$ where dQ_{rev}^{α} is the reversible heat transferred to or from the system at the temperature T^{α} **FOR THE REVERSIBLE MODEL**, not the actual process. For closed systems that depend on only P, V and T we can use any of the following relationships for the **SYSTEM**. Be sure you know how to derive these equations!

$$dS^{\alpha} = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$dS^{\alpha} = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$dS^{\alpha} = \frac{C_v}{T} \left(\frac{\partial T}{\partial P} \right)_V dP + \frac{C_P}{T} \left(\frac{\partial T}{\partial V} \right)_P dV$$

$$\Delta S^{\alpha} = \frac{\Delta_{phase1}^{phase2} H_{Trans}}{T_{Trans}} \quad \text{Phase Transitions}$$

Surroundings Entropy Change

This is a bit tricker. To begin with, assume the walls surrounding the **system** are diathermal so the system can exchange heat with the surroundings. Remember the walls surrounding the composite are adiabatic and rigid and that the heat reservoir part of the surroundings has an infinite heat capacity so that T^{β} is constant no matter how much heat is exchanged with α. We also assume the 'work reservoir' has an infinite capacity in the sense that the surroundings do not change irrespective of how much work is done on or by the system. From the first law we have:

$dU^{\beta} = dQ^{\beta} + dW^{\beta} = dQ^{\beta}$ because $dW^{\beta} = 0$ due to the constant volume property of β.

This means dQ^{β} is a state function i.e., dQ^{β} is exact because dU^{β} is exact, which in turn implies,

1) dQ^{β} (rev) = dQ^{β} (actual)

in other words, the **actual** amount of heat exchanged between the system and the surroundings is the same irrespective as to how the process was carried out, i.e., reversibly or irreversibly. That is, from the viewpoint of the surroundings, it does not matter if the process is reversible or irreversible because the amount of heat transferred depends only on the end points of the process.

Now, the composite has an adiabatic wall so

2)   dQ (composite) = dQ^{β} (actual) + dQ^{α} (actual) = 0

where we note that we are talking about the **actual** process, not the **model** process for the system! From 2) we have

dQ^{β} (actual) = $-dQ^{\alpha}$ (actual)   or, on using 1) above, we have,

dQ^{β} (rev) = $-dQ^{\alpha}$ (actual)   which is the result we are after

So finally we can write, using the formal definition of the entropy,

$$\Delta S^{\beta} \equiv \int \frac{dQ^{\beta}_{rev}}{T^{\beta}} = -\int \frac{dQ^{\alpha}_{actual}}{T^{\beta}}$$

which is a splendid result for now we can, in principle at least, calculate dQ^{α}_{actual} using the first law for the **system**, not the **surroundings**. Thus, we have a recipe for calculating the entropy change in the surroundings by asking ourselves 'how much heat was actually transferred between α and β in the REAL process' and at what temperature? Then, if you are able to calculate the ratio, $\dfrac{dQ^{\alpha}_{actual}}{T^{\beta}}$ you can calculate ΔS^{β}.

Comments

- If the **system** has an adiabatic wall and the process is irreversible then $dQ^{\alpha}_{actual} = 0$ so $dS_{surr} = 0$ so now $dS_{total} = dS_{system} \geq 0$ because $dQ^{\alpha}_{rev\,model} \neq 0$. Remember, the reversible model and the actual process share only the end points of the process – otherwise the two processes will always be quite different physically!

- If the **system** has an diathermal wall and the process is irreversible then neither dS_{sys} or dS_{surr} will be zero and their sum will be > 0. Note that either entropy can be negative, but not both.

- If the actual process is **reversible** and the system wall is diathermal so $T^{\beta} = T^{\alpha}$, then

$$dS^{\alpha} = \frac{dQ^{\alpha}_{rev}}{T^{\alpha}}$$

$$dS^{\beta} = -\frac{dQ^{\beta}_{actual}}{T^{\beta}} = -\frac{dQ^{\alpha}_{rev}}{T^{\alpha}}$$

and $dS_{total} = 0$

- Likewise, if the actual process is **reversible** and the system wall is adiabatic, then, as we have seen above,

$dS^{\beta} = 0$ and

$$dS^{\alpha} = \frac{dQ^{\alpha}_{rev}}{T^{\alpha}} = 0 \text{ because } dQ^{\alpha}_{rev} = 0 \text{ so again } dS_{total} = 0$$

The point is, reversible processes are indistinguishable from equilibrium so $dS_{total} = 0$ always, as the 2nd law asserts.

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1/27/2010

Third Law Computations

Standard States for Entropy - Pure Substances:

a) Condensed Phases: most stable form at 1 bar.

b) Gas: Hypometical ideal gas at 1 bar.

Standard Entropy of Reaction

$$\Delta S_R^{\ominus}(\$) = \sum_i \nu_i S_i^{\ominus}(\$)$$

where the $S_i^{\ominus}(\$)$ are the absolute entropies relative to $T = 0$ for which $S_i^{\ominus}(0) \equiv \emptyset$ (most stable form etc.)

Entropy Calculations

Condensed Phases

a) From $T = 0K$ to $T = T_1$

Need: Θ_D from $C_p(T) = \dfrac{12\pi^4}{5} R \left(\dfrac{T}{\Theta_D}\right)^3$

Compute Θ_D from the $C_p(T_{min})$ & assumes it holds all the way from $0K$ to T_1.

b) From T_1 to T_{final}

$$\Delta S(T_{final}) = \sum_{\sigma} \int_{T_1}^{T_\sigma} \frac{C_p(\sigma)}{T} dT \quad \text{where } \sum_{\sigma} \text{ is over each phase } \sigma.$$

c) Phase Transitions

$$\Delta S(\sigma_i \rightarrow \sigma_j) = \sum_\sigma \frac{\Delta_{\sigma_i}^{\sigma_j} H_T}{T_T} \quad \text{where } \Delta H \text{ is the enthalpy of the transition at the temp. } T_T$$

Overall:

$$S(T') = a + b + c + \text{gas phase correction for non-ideal}^{\circledR}$$

$\circledast$ $S_{IG}(P=1) - S_{RG}(P=1) = R\left[B'(T) + T \dfrac{dB'(T)}{dT} \right]$ for $\dfrac{PV}{RT} = 1 + B'(T) P$