ChemE 2200 – Chemical Thermodynamics Lecture 9

Today:

The Gibbs Energy, *G*.

The Parameters of Thermodynamics – Physical Observables and Theoretical Concepts.

The Maxwell Relations.

Defining Question:

What is the difference between Maxwell Relations and Useful Relations?

Reading for Today's Lecture:

McQuarrie & Simon, Chapter 23.1-23.3

Reading for Thermodynamics Lecture 10:

McQuarrie & Simon, Chapter 22.3-23.8

1st Prelim

Tuesday, March 11, 7:30 – 9:30 p.m.

245 Olin Hall

Covers –
- Atomic Orbitals
- Molecular Orbitals
- Molecular Spectroscopy
- Electrons in Solids
- Classical Thermodynamics through 1st Law

Covers –
- Lectures through 1st half of Monday, 2/24 (Lecture T4)
- Homework through Homework 5
- Calculation Sessions through Calculation Session 5

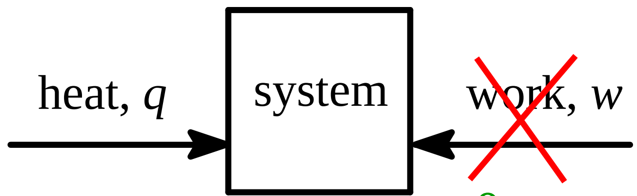
You may use a hand-written, double-sided reference sheet.
Reference sheets will be submitted with the Prelim.
Reference sheets will be returned Wednesday, March 12.

Recap

The 2nd Law of Thermodynamics: $\Delta S_{\text{overall}} > 0$ for a spontaneous process.

$$dS \geq \frac{\delta q}{T}$$ The Clausius Inequality

Closed system:



Assume constant volume.

$w = P\Delta V = 0$ for only PV work.

$$dU = \delta q + \cancelto{0}{\delta w}$$

$$dU = \delta q \leq TdS$$

$$dU - TdS \leq 0$$ for spontaneous processes.

Extremes: If $dU = 0$, $TdS \geq 0$ for a spontaneous process.

If $dS = 0$, $dU \leq 0$ for a spontaneous process.

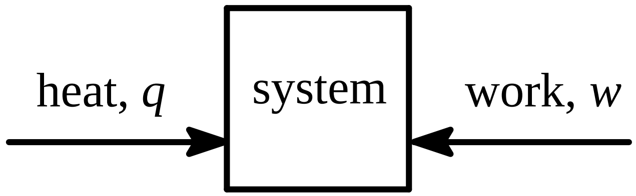
Important: System U decreases because heat transfers to the surroundings.

$\Rightarrow \Delta S_{\text{surroundings}} > 0$ Process is spontaneous because *entropy increases*.

Helmholtz Energy: $\Delta A = \Delta U - T\Delta S = w_{\max}$

Chaos tax on conversion of internal energy to work.

Spontaneity – Closed System at Constant Pressure



$dU = \delta q + \delta w$ substitute $\delta w = -PdV$

$dU = \delta q - PdV$ substitute $TdS \geq \delta q$

$dU \leq TdS - PdV$

$dU + PdV - TdS \leq 0$

Define Gibbs Energy $\equiv G = U + PV - TS$

$$dG = d(U + PV - TS) = dU + PdV + \cancelto{0}{VdP} - TdS - \cancelto{0}{SdT}$$

assume constant T and constant P. $dG = dU + PdV - TdS$

$$\boxed{dG \leq 0 \text{ for spontaneous processes at constant } T \text{ and } P.}$$

Internal Energy, Enthalpy, Helmholtz Energy, and Gibbs Energy

The Gibbs Energy is another Legendre Transform

$+PV \rightarrow$

$-TS \downarrow$

U internal energy	H enthalpy
A Helmholtz energy	G Gibbs energy

T and S are an energy conjugate pair.

(intensive variable) × (extensive variable)

product has dimensions of energy.

TS is an *heat* transform

P and V are an energy conjugate pair.

(intensive variable) × (extensive variable)

product has dimensions of energy.

PV is a *work* transform

$$H = U + PV$$

$$A = U - TS$$

$$G = U + PV - TS$$

$$G = A + PV$$

$$\boxed{G = H - TS}$$

A useful transform

Change in Gibbs Energy, ΔG, is maximum non-PV work

Start with the definitions of H and U. $dH = dU + d(PV)$ $dU = \delta q + \delta w$

$$dH = \delta q + \delta w + d(PV)$$

$$dG = dH - TdS$$

$$dG = \delta q + \delta w + d(PV) - TdS$$

Assume reversible processes: $\delta w = \delta w_{\text{rev}}$, $\delta q = \delta q_{\text{rev}} = TdS$

$$dG = \cancel{TdS} + \delta w_{\text{rev}} + d(PV) - \cancel{TdS}$$

$$dG = \delta w_{\text{rev}} + PdV + V\cancelto{0}{dP}$$

Assume constant P: $dG = \delta w_{\text{rev}} + PdV$

Divide work into PV work and non-PV work: $\delta w_{\text{rev}} = -PdV + \delta w_{\text{non-}PV\text{, rev}}$

$$dG = -\cancel{PdV} + \delta w_{\text{non-}PV\text{, rev}} + \cancel{PdV}$$

$$\boxed{dG = \delta w_{\text{non-}PV\text{, rev}}}$$

Change in Gibbs Energy, ΔG, is maximum non-PV work

$$\boxed{dG = \delta w_{\text{non-}PV\text{, rev}}}$$

Non-PV work:

electrical work: $w = (\text{charge}) \times (\Delta\text{voltage})$

gravitational work: $w = (\text{mass}) \times \text{g} \times (\Delta\text{height})$

magnetic work: $w = (\text{magnetic dipole}) \times \text{B} \times (\Delta\text{distance})$

shaft work: $w = (\text{torque}) \times (\Delta\text{angular distance})$

The Gibbs Energy for Spontaneity of Chemical Reactions

glucose oxidation: $C_6H_{12}O_6(s) \ + \ 6O_2(g) \rightarrow 6CO_2(g) \ + 6H_2O(l)$

$\Delta\overline{H}^0_{\text{formation}}$	-1271	0	-393.5	-285.8 kJ/mol	Table 19.2
$\overline{S}^{\,0}$	$+209.2$	$+205.2$	$+213.8$	$+70.0$ J/(K·mol)	Table 21.2

$$\Delta\overline{H}^0_{\text{rxn}} = \sum_{\text{products}} \Delta\overline{H}^0_{\text{formation}} - \sum_{\text{reactants}} \Delta\overline{H}^0_{\text{formation}}$$

$$= 6(-393.5) + 6(-285.8) - (-1271 + 6(0)) = -2804.8 \text{ kJ/mol}$$ exothermic

$$\Delta\overline{S}_{\text{rxn}} = \sum_{\text{products}} \overline{S}^{\,0} - \sum_{\text{reactants}} \overline{S}^{\,0}$$

$$= 6(213.8) + 6(70.0) - (209.2 + 6(205.2)) = +262.4 \text{ J/(K·mol)}$$ disorder increases

$$\Delta\overline{G}^0_{\text{rxn}} = \Delta\overline{H}^0_{\text{rxn}} - T\Delta\overline{S}^0_{\text{rxn}}$$

$$= -2804.8 \text{ kJ/mol} - (+78.2 \text{ kJ/mol}) = -2883.0 \text{ kJ/mol}$$ spontaneous!

at constant P and constant T (298 K)

Note: The Gibbs energy change of a chemical reaction is the change in Gibbs energy for pure separated reactants in their standard state to pure separated products in their standard state.

The Gibbs energy of mixing (and unmixing) is not included.

The Gibbs Energy for Spontaneity of Chemical Reactions

glucose oxidation: $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

$\Delta\overline{G}^0_{\text{formation}}$ –910.52 0 –394.39 –237.14 kJ/mol

Table 26.1
McQ & S
p. 1057

$$\Delta\overline{G}^0_{\text{rxn}} = \sum_{\text{products}} \Delta\overline{G}^0_{\text{formation}} - \sum_{\text{reactants}} \Delta\overline{G}^0_{\text{formation}}$$

$$= 6(-394.39) + 6(-237.14) - (-910.52 + 6(0)) = -2878.7 \text{ kJ/mol}$$

spontaneous!

at constant *P* and constant *T* (298 K)

Compare to –2883.0 kJ/mol from previous slide.

0.15% difference. Typical.

The Gibbs Energy for Spontaneity of Chemical Reactions

ammonia synthesis: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

At what temperature is the reaction spontaneous at 1 bar?

$$\Delta\overline{H}^0_{rxn} = -92\ \text{kJ/mol}$$

$$\Delta\overline{S}^0_{rxn} = -198.5\ \text{J/(K}\cdot\text{mol)}$$

$$\Delta\overline{G}^0_{rxn} = \Delta\overline{H}^0_{rxn} - T\Delta\overline{S}^0_{rxn}$$

Spontaneous at $\Delta\overline{G}^0_{rxn} = 0$

$$0 = \Delta\overline{H}^0_{rxn} - T\Delta\overline{S}^0_{rxn}$$

$$T = \frac{\Delta\overline{H}^0_{rxn}}{\Delta\overline{S}^0_{rxn}} = \frac{-92.0\ \text{kJ/mol}}{-198.5\ \text{J/(K}\cdot\text{mol)}}(1000\ \text{J/kJ}) = \boxed{463\ \text{K}}$$

The Gibbs Energy for Spontaneity of Chemical Reactions

$\boxed{dG \leq 0 \text{ for spontaneous processes at constant } T \text{ and } P.}$

$$\Delta \overline{G}^0_{\text{rxn}} = \Delta \overline{H}^0_{\text{rxn}} - T\Delta \overline{S}^0_{\text{rxn}}$$

The 2nd Law of Thermodynamics: $\Delta S_{\text{overall}} > 0$ for a spontaneous process.

$\Delta S_{\text{rxn}} > 0$ increases entropy. Contributes to spontaneity.

$\Delta H_{\text{rxn}} < 0$ increases entropy by heat transfer to surroundings to keep temperature constant. Contributes to spontaneity.

	$\Delta H_{\text{rxn}} < 0$ exothermic	$\Delta H_{\text{rxn}} > 0$ endothermic
$\Delta S_{\text{rxn}} > 0$ disorder increases	spontaneous at all temperatures	spontaneous at high temperatures
$\Delta S_{\text{rxn}} < 0$ disorder decreases	spontaneous at low temperatures	not spontaneous at any T*

*We will see later that all reactions go forward an infinitesimal fractional conversion.

Fundamental Equation for the Gibbs Energy, *dG*

Recall: $dU = TdS - PdV$ fundamental equation for *dU*

$dA = -SdT - PdV$ fundamental equation for *dA*

$dH = TdS + VdP$ fundamental equation for *dH*

Start with a definition of *G*: $G = H - TS$

$$dG = dH - TdS - SdT$$

$$dG = (\cancel{TdS} + VdP) - \cancel{TdS} - SdT$$

$$\boxed{dG = VdP - SdT}$$ fundamental equation for *dG*

The natural variables of Gibbs energy are temperature and pressure.

J. Willard Gibbs (1839-1903)

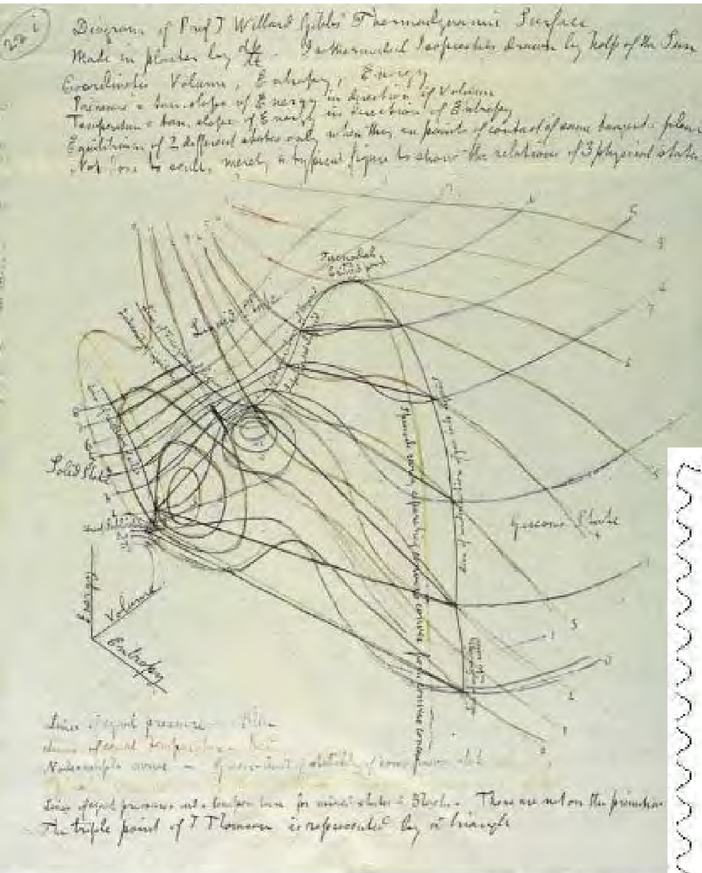
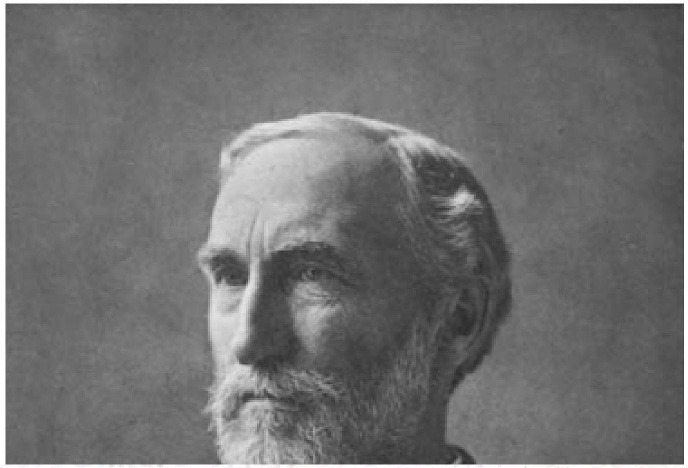
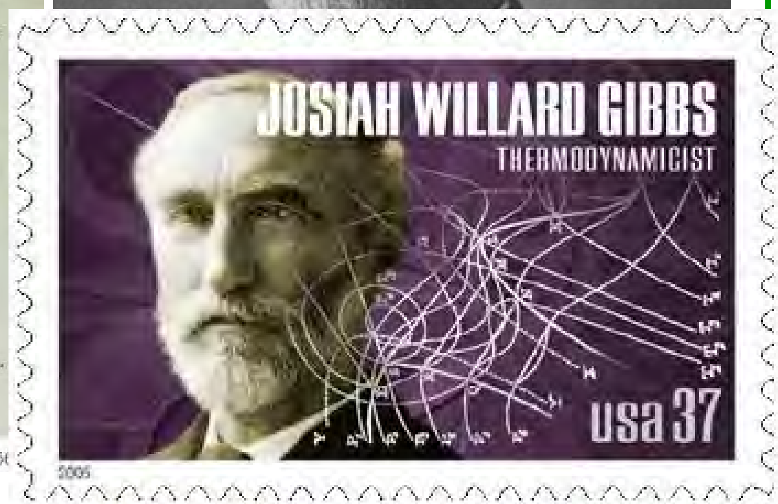
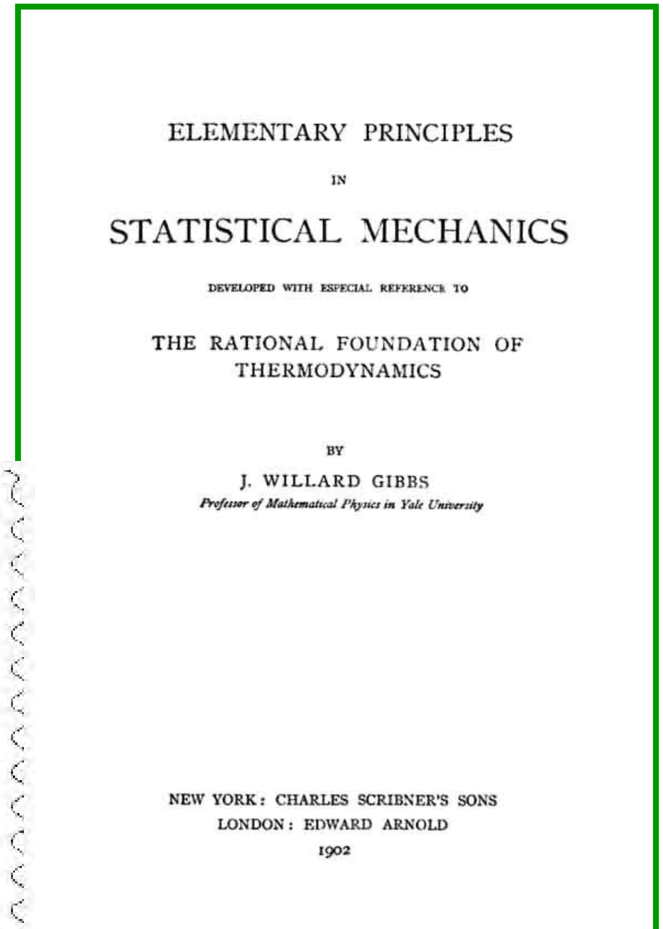


Plate IV. Diagram of the lines on Gibbs' thermodynamic surface, 8 July 1875 (Number 5







ELEMENTARY PRINCIPLES

IN

STATISTICAL MECHANICS

DEVELOPED WITH ESPECIAL REFERENCE TO

THE RATIONAL FOUNDATION OF THERMODYNAMICS

BY

J. WILLARD GIBBS

Professor of Mathematical Physics in Yale University

NEW YORK: CHARLES SCRIBNER'S SONS
LONDON: EDWARD ARNOLD
1902

Elevated Physical Chemistry from an empirical subject to a mathematically rigorous deductive science.

Created Vector Calculus.

With Ludwig Boltzmann and James Clerk Maxwell created Statistical Mechanics

"The greatest mind in American history" Albert Einstein

Practical Equations from Fundamental Equations

The parameters of thermodynamics

$$\left.\begin{matrix} P \\ \overline{V} \\ T \end{matrix}\right\} \text{ physical observables}$$

$$\left.\begin{matrix} U \\ S \\ H = U + PV \\ A = U - TS \\ G = H - TS \end{matrix}\right\}$$

thermodynamic abstract concepts.

essential for analysis
but cannot be measured.

Goal: Express 'conceptual variables' in terms of physical observables.

Example: $dU = TdS - PdV$ fundamental equation for dU

How to evaluate?

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

practical equation for dU

Can be evaluated with a physical parameter (C_V)
and an equation of state, such as $PV = nRT$.

How to derive practical equations from fundamental equations? The Maxwell Relations!

The Maxwell Relations

Fundamental equation for $U(S,V)$: $dU = TdS - PdV$

Total derivative of $U(S,V)$: $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

Thus: $\left(\frac{\partial U}{\partial S}\right)_V = T$ $\left(\frac{\partial U}{\partial V}\right)_S = -P$

substitute

Because the derivative is exact, Euler's Theorem provides that

substitute

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial U}{\partial V}\right)_S$$

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

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

A Maxwell Relation

Analogously, the other fundamental equations yield Maxwell Relations.

The Maxwell Relations

$$U(S,V):\ dU = TdS - PdV \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$H(S,P):\ dH = TdS + VdP \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$A(T,V):\ dA = -SdT - PdV \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$G(T,P):\ dG = -SdT + VdP \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

The goal was practical equations, but Maxwell Relations are also useful.

$$dS = -\left(\frac{\partial V}{\partial T}\right)_P dP \ \text{ at constant } T \quad \Rightarrow \quad \Delta S = -\int_{P_1}^{P_2}\left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\text{assume } V = \frac{nRT}{P} \qquad \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\right)_P \frac{nRT}{P} = \frac{nR}{P}$$

$$\Delta S = -\int_{P_1}^{P_2}\frac{nR}{P}dP = -nR\ln\frac{P_2}{P_1} \quad \text{for an ideal gas at constant } T.$$

The Equations of Thermodynamics

energy	definition	natural variables	fundamental equation	Maxwell relation	practical equation
internal	$U = q + w$	S and V	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$
Helmholtz	$A = U - TS$	T and V	$dA = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$	$dS = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$
enthalpy	$H = U + PV$	S and P	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$
Gibbs	$G = H - TS$	T and P	$dG = -SdT + VdP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$	$dS = \frac{C_P}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP$

need C_P or C_V and an equation of state.

Properties of matter

$\left(\frac{\partial U}{\partial T}\right)_V = C_V$ heat capacity at constant volume

$\left(\frac{\partial H}{\partial T}\right)_P = C_P$ heat capacity at constant pressure

$\left(\frac{\partial T}{\partial P}\right)_H = \mu$ Joule-Thomson coefficient

$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha$ coefficient of thermal expansion

$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \kappa_T$ isothermal compressibility

$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \kappa_S$ adiabatic compressibility

Some Useful Relations

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

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

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

example: provides C_V dependence on V.

$$\bar{C}_P = \bar{C}_V + T\left(\frac{\partial P}{\partial T}\right)_{\bar{V}}\left(\frac{\partial \bar{V}}{\partial T}\right)_P$$

$$\boxed{\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V}$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]$$

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

A Practical Equation for dU

Recall our goal: To calculate the change in internal energy with changes in temperature and volume.

Write the total derivative of $U(T,V)$: $$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

A property of matter: $$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

$\left(\frac{\partial U}{\partial V}\right)_T$? Use the energy with natural variables V and T.

$$A = U - TS$$

Write the partial derivative with respect to V at constant T.

$$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - \cancel{\left(\frac{\partial T}{\partial V}\right)_T}^{\,0} S - T\left(\frac{\partial S}{\partial V}\right)_T$$

A Useful Relation

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

A Maxwell Relation

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

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

Useful Relations

The source of the useful relation on the previous slide: $\left(\frac{\partial A}{\partial V}\right)_T = -P$

Start with the fundamental equation for dA:

$$dA = -SdT - PdV$$

Write the total derivative for $A(T,V)$:

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

Equate prefactors of dV: $\left(\frac{\partial A}{\partial V}\right)_T = -P$

Derive Useful Relation $\left(\frac{\partial G}{\partial P}\right)_T = V$

Defining Question:

What is the difference between Maxwell Relations and Useful Relations?

All Maxwell Relations are useful, but not all Useful Relations are Maxwell Relations.

Multivariable Calculus – Euler's Theorem

Given a quantity h that is a function of two independent variables, x and y. That is, $h = h(x,y)$. The differential dh defined as

$$dh = f(x,y)dx + g(x,y)dy$$

is an exact differential if

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial g}{\partial x}\right)_y$$

Note that

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

is an exact differential because Euler's theorem requires that

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

Multivariable Calculus – Partial Derivatives

Partial Derivatives. Consider a set of four variables, w, x, y, and z, such that only two are independent. For example for one mole of a gas, the set of variables is P, V, T, and U. We may designate V and T as the independent variables, thus $P = P(V,T)$ and $U = U(V,T)$.

Assume $z = z(x,y)$.

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

$$\left(\frac{\partial z}{\partial w}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial w}\right)_y \qquad \text{chain rule}$$

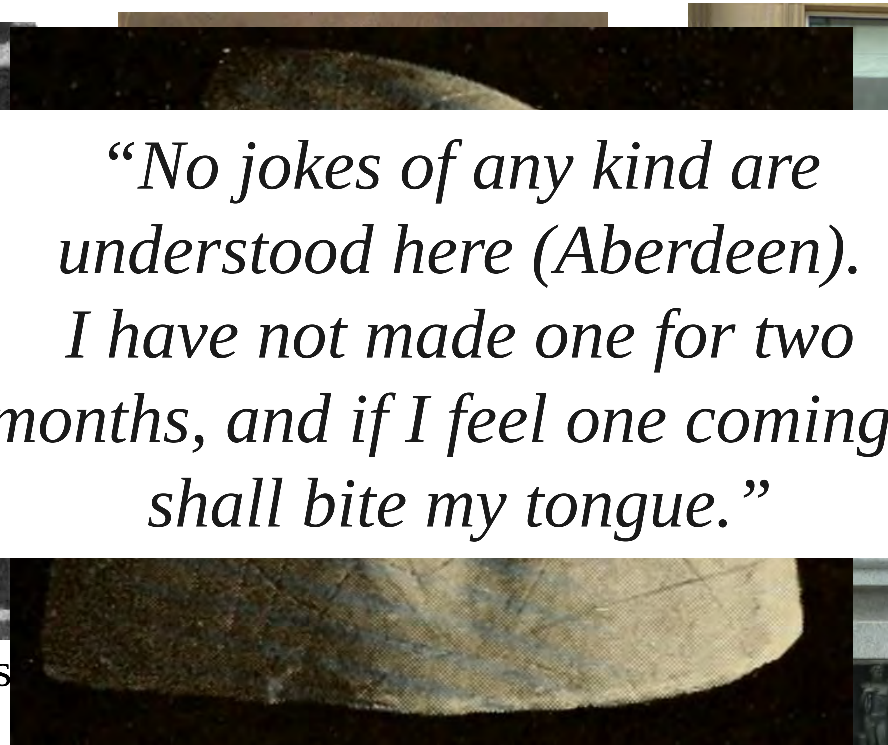
$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1 \qquad \text{reciprocal rule}$$

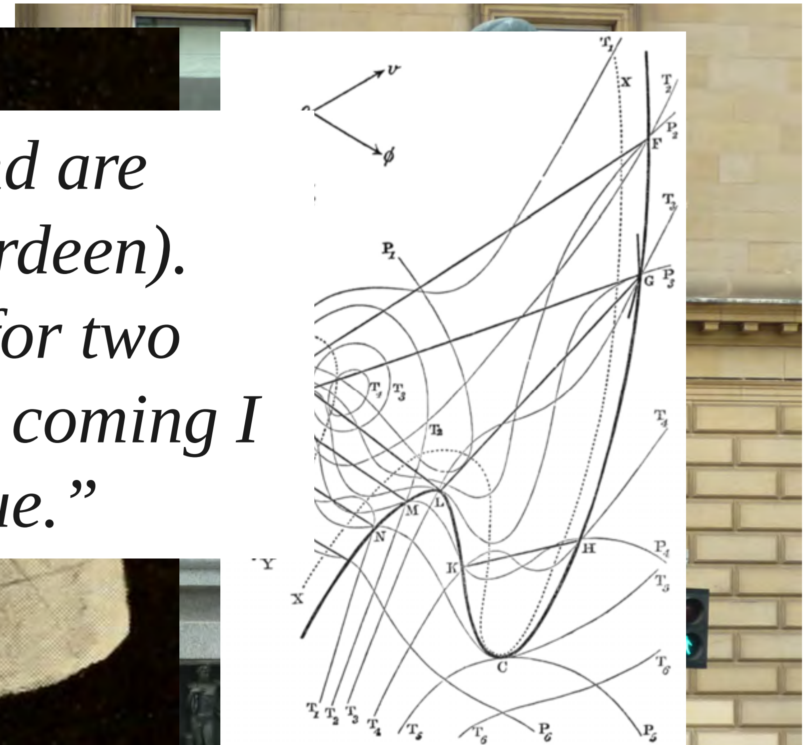
$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \qquad \text{cyclic rule}$$

$$\left(\frac{\partial z}{\partial x}\right)_w = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_w$$

James Clerk Maxwell (1831-1879)

At Cambridge in his 20s





"No jokes of any kind are understood here (Aberdeen). I have not made one for two months, and if I feel one coming I shall bite my tongue."

Maxwell's Legacy:

- Maxwell's Equations for Electromagnetism
- Colour Vision & Colour Photography
- Maxwell-Boltzmann Distribution
- Kinetic Theory of Gases
- Control Theory
- Maxwell's Equations for Thermodynamics
- Quirky Sense of Humor