Welcome to PChem!

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- Instructor name: T. Pradeep
- Instructor's email ID: **pradeep@iitm.ac.in**
- Course material will be available on the moodle site: https://courses.iitm.ac.in/
- The site contains not only course materials, but other interesting aspects of teaching/learning, assignments, wiki on thermodynamics, etc.
- All Monday classes are tutorials

MIDSEM EXAM (March 2015, beginning)

portions from:

Theoretical Chemistry &

Physical Chemistry

Assessment Pattern(PChem): Problem solving
Numerical, Derivations, Justifications
Plotting graphs

Rules and Policies

- I shall come a minute or two before the class time. I except you to follow the same practice.
- Late comers not more than 5 minutes will not be allowed to enter the class
- I encourage questions in the class

Text Books for References

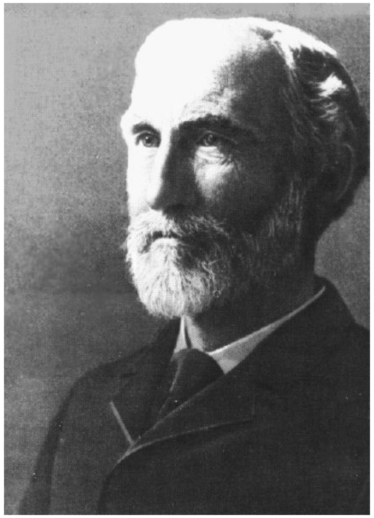
Kuhn Hans, Försterling Horst-Dieter and Waldeck David H, *Principles of Physical Chemistry*, 2nd Ed., Wiley (2009).

P. W. Atkins, Physical Chemistry, Seventh Edition, Oxford University Press, 1998.

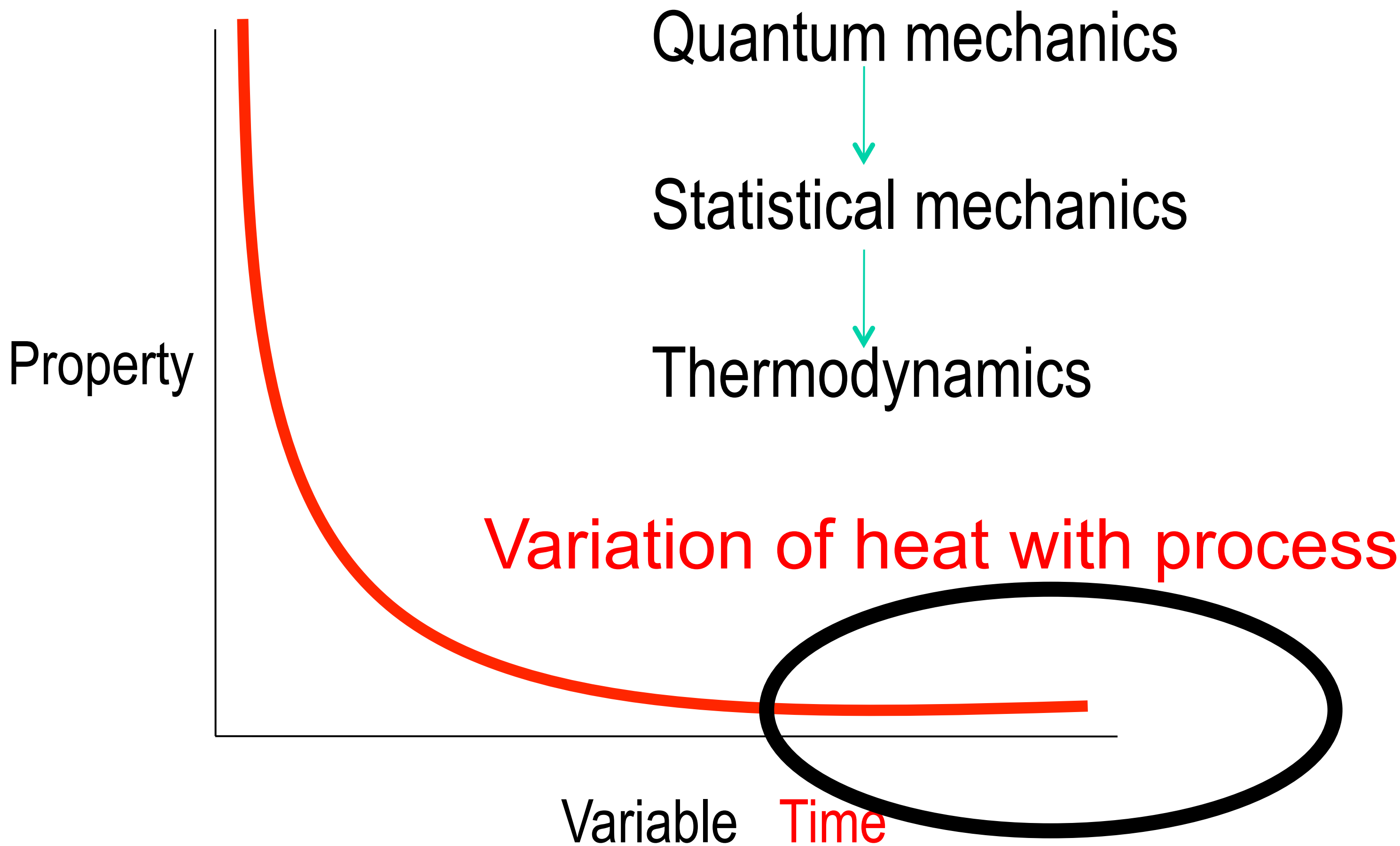
Silbey, R. J., Alberty, R. A., Bawendi, M. G. *Physical Chemistry*, Fourth Edition, John Wiley, 2006.

Fundamental Equations and Maxwell Relations

Lecture 1



Josiah Willard Gibbs 1839-1903


Quantum mechanics
Statistical mechanics
Thermodynamics
Property
Variation of heat with process
Variable
Time

- **Learning Outcome (Lecture 01)**

At the end of this class, you will be able to:

Explain how thermodynamic properties can be related using Maxwell's relations

Fundamental equation for internal energy

$dU = \partial q + \partial w$ First law

$dS \geq \frac{\partial q}{T}$ Second law

For reversible PV work, $\partial w = -PdV$ and $dS = \frac{\partial q}{T}$

$\Rightarrow$ $dU = TdS - PdV$ (good for both reversible and irreversible process)

Conjugate variables

$$dU = TdS - PdV + \sum_{i=1}^{N_s} \mu_i dn_i \qquad \textbf{(FE-1)}$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{i=1}^{N_S} \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j \neq n_i} dn_i$$

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

Natural variables

The function,

$$df = g\,dx + h\,dy$$

is exact, if:

$$(\partial g/ \partial y)_x = (\partial h/ \partial x)_y$$

Test for exactness- Euler's theorem

$dU = TdS - PdV$ (1) *Fundamental equation of a pure system*

Applicable to both reversible and irreversible.

$U = f(S,V)$ why only these two?

$dU = (\partial U/ \partial S)_V dS + (\partial U/ \partial V)_S dV$ (2)

Using thermodynamic equations

Compare (1) and (2)

$(\partial U/ \partial S)_V = T$ (3)

$(\partial U/ \partial V)_S = -P$ (4) **Thermodynamics give unusual relations!**

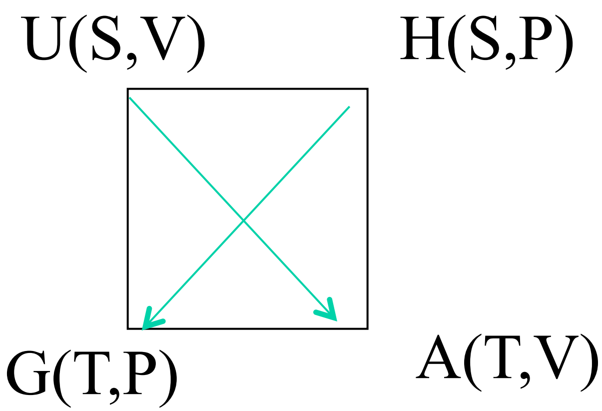
From (3), $(\partial U^2/ \partial V \partial S) = (\partial T/ \partial V)_S$

From (4), $(\partial U^2/ \partial S \partial V) = -(\partial P/ \partial S)_V$

As dU is an exact differential,

$(\partial T/\partial V)_S = -(\partial P/ \partial S)_V$ **Maxwell relation (1)**

$$dU = TdS - PdV$$
$$dH = TdS + VdP$$
$$dA = -SdT - PdV$$
$$dG = -SdT + VdP$$



Maxwell relations

$$(\partial T/ \partial V)_S = -(\partial P/ \partial S)_V$$
$$(\partial T/ \partial P)_S = (\partial V/ \partial S)_P$$
$$(\partial S/ \partial V)_T = (\partial P/ \partial T)_V$$
$$-(\partial S/ \partial P)_T = (\partial V/ \partial T)_P$$

The first two relations are for constant entropy, ie. adiabatic processes. Rate of change of temperature with volume and pressure are the quantities discussed. The latter two relations are for constant temperature, ie. isothermal processes. Entropy change as a function of volume and pressure can be related to changes in pressure and volume.

How can such relations be tested?

Thermodynamic equation of state

The ideal gas law and van der Waals equation are relations between P, V and T. These are based on some data and extrapolations and speculations on the molecular dimensions and interactions between molecules.

Is there a more generalised law describing equilibrium?

Thermodynamics gives one.

dU = TdS – PdV is the condition of equilibrium.

Let us write,

$(\partial U)_T = T(\partial S)_T - P(\partial V)_T$

Divide by $(\partial V)_T$

$(\partial U/\partial V)_T = T(\partial S/\partial V)_T - P$

U and S are functions of T and V.
Thus, the above relation relates P with functions of T and V.
Therefore, this is an equation of state.

Using value of $(\partial S/\partial V)_T$ from Maxwell's relation $(\partial S/ \partial V)_T = (\partial P/ \partial T)_V$,

$$\mathbf{P = T(\partial P/\partial T)_V - (\partial U/\partial V)_T}$$

Taking,

$$dH = TdS + VdP$$

$$(\partial H/\partial P)_T = T(\partial S/\partial P)_T + V$$

Using Maxwell relation, $-(\partial S/ \partial P)_T = (\partial V/ \partial T)_P$

$$\mathbf{V = T(\partial V/\partial T)_P + (\partial H/\partial P)_T}$$

This equation expresses volume as a function of temperature and pressure.

These relations are applicable to any substance.

Maxwell relations

$$(\partial T/ \partial V)_S = -(\partial P/ \partial S)_V$$

$$(\partial T/ \partial P)_S = (\partial V/ \partial S)_P$$

$$(\partial S/ \partial V)_T = (\partial P/ \partial T)_V$$

$$-(\partial S/ \partial P)_T = (\partial V/ \partial T)_P$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{i=1}^{N_S} \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j \neq n_i} dn_i$$

No end to equations!