Some terms that must be understood

Microscopic Variable

Macroscopic Variable
<table>
<thead>
<tr>
<th>Extensive ($\propto N$)</th>
<th>Intensive ($\neq f(N)$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$ volume</td>
<td>$P$ pressure</td>
</tr>
<tr>
<td>$A$ area</td>
<td>$S$ surface tension</td>
</tr>
<tr>
<td>$L$ length</td>
<td>$F$ tension</td>
</tr>
<tr>
<td>$P$ polarization</td>
<td>$E$ electric field</td>
</tr>
<tr>
<td>$M$ magnetization</td>
<td>$H$ magnetic field</td>
</tr>
<tr>
<td>$U$ internal energy</td>
<td>$T$ temperature</td>
</tr>
</tbody>
</table>
Adiabatic Walls

Equilibrium

Steady State

Diathermic Walls

Complete Specification:

Independent and Dependent Variables
Equation of State

\[ PV = NkT \]

\[ V = V_0(1 + \alpha T - \kappa_T P) \]

\[ M = cH/(T - T_0) \quad T > T_0 \]

In Equilibrium with Each Other
OBSERVATIONAL FACTS

"0th Law"

if A \rightleftharpoons C and B \rightleftharpoons C

then A \rightleftharpoons B
"Law 0.5?" Many macroscopic states of B can be in equilibrium with a given state of A

\[
Y_B = f(X_B)
\]

Also, \(X_A, Y_A\)
THEOREM  A "predictor" of equilibrium $h(X, Y, \ldots)$ exists

- only in equilibrium
- state variable
- many states, same $h$
- different systems,
  different functional forms
- value the same if systems in equilibrium

![Diagram showing the locus of constant $h$]
\[ X_A, Y_A, X_C, Y_C \text{ all free} \]

\[ \text{equilibrium} \]

\[ X_C = f_1(Y_C, X_A, Y_A) \]

\[ F_1(X_C, Y_C, X_A, Y_A) = 0 \]

\[ [P_C = P_A V_A/V_C] \]

\[ [P_C V_C - P_A V_A = 0] \]
\[ X_B = g(Y_B, X_C, Y_C) \]

\[ F_2(X_C, Y_C, X_B, Y_B) = 0 \]

Solve for \( X_C \)

\[ X_C = f_2(Y_C, X_B, Y_B) \]

Same value as before
\[ f_1(Y_C, X_A, Y_A) = X_C = f_2(Y_C, X_B, Y_B) \]

\[ [ P_A V_A / V_C = P_B V_B / V_C ] \]

equilibrium due to 0th law

\[ \Rightarrow F_3(X_A, Y_A, X_B, Y_B) = 0 \]

\[ 1 + 2 \Rightarrow F_3 \text{ factors} \]

\[ Y_C \text{ drops out} \]
For this equilibrium condition

\[ h( X_A, Y_A ) = \text{constant} = h( X_B, Y_B ) \]

\[ [ P_A V_A = P_B V_B ] \]
Empirical Temperature: $t$

- Low density gas
- $PV/N =$ constant'

Graphs showing $Y$ versus $X$ and $P$ versus $V$ with points 1 and 2 indicating changes in state.
we could possible alternative

- Define $t \equiv c_g (PV/N)$

- Use to find isotherms in other systems

- Then in a simple paramagnet
  
  $t = c_m (M/H)^{-1}$

$\Rightarrow$ Many possible choices for $t$

$t' \equiv c_g' (PV/N)^\alpha$

$t' = c_m' (M/H)^{-\alpha}$
PV = Nkt → t = PV/Nk
\[ t' = \left(\frac{PV}{Nk}\right)^2 \]
\[ t'' = \sqrt{\frac{PV}{Nk}} \]
Work

\[ \text{d}W \equiv \text{differential of work done on the system} \]

\[ = - (\text{work done by the system}) \]

Hydrostatic system

\[ \text{d}W = -P\text{d}V \]

\[ \text{d}W = F\text{d}x = (PA)(-\text{d}V/A) = -P\text{d}V \]
Wire
\[ \delta W = F dL \]

Surface
\[ \delta W = S dA \]

P pushes, \( F \) pulls

\[ \delta W = F dx = (F)(dL) = FdL \]

\[ \delta W = F dx = (SL)(dA/L) = SdA \]
Chemical Cell (battery)
\[ \delta W = E_{\text{EMF}} \delta Z_{\text{CHARGE}} \]

Electric charges
\[ \delta W = E \delta P \]

Magnetic systems
\[ \delta W = H \delta M \]

Field in absence of matter as set up by external sources. Does not include energy stored in the field itself in the absence of the matter.
• All differentials are extensive

• Only -PdV has a negative sign

• Good only for quasistatic processes

\[ \Delta W = \int_{a}^{b} dW \] depends on the path

\[ \Rightarrow W \] is not a state function
\[ dW = YdX \]

depends on \( Y(X) \)
(a) $W_{1\rightarrow 2} = -P_1(V_2 - V_1) = P_1(V_1 - V_2)$

(b) $W_{1\rightarrow 2} = -P_2(V_2 - V_1) = P_2(V_1 - V_2)$

(c) $W_{1\rightarrow 2} = -\int_1^2 P(V) \, dV = -\int_1^2 \frac{NkT}{V} \, dV = -NkT \int_1^2 \frac{dV}{V}$

$$= -NkT \ln \frac{V_2}{V_1} = NkT \ln \frac{V_1}{V_2} = P_1 V_1 \ln \frac{V_1}{V_2}$$
I) 3 variables, only 2 are independent

\[ F(x, y, z) = 0 \]

\[ \Rightarrow x = x(y, z), \quad y = y(x, z), \quad z = z(x, y) \]

\[ \Rightarrow \left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_z}, \quad \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1 \]
Given some $W = W(x, y, z)$ where only 2 of the 3 variables in the argument are independent,
then along a path where $W$ is constrained to be constant

$$\left(\frac{\partial x}{\partial y}\right)_W \left(\frac{\partial y}{\partial z}\right)_W \left(\frac{\partial z}{\partial x}\right)_W = 1$$
then it follows that \( \left( \frac{\partial x}{\partial y} \right)_w = \frac{\left( \frac{\partial x}{\partial z} \right)_w}{\left( \frac{\partial y}{\partial z} \right)_w} \)

II) State function of 2 independent variables

\[ S = S(x, y) \]

\[ dS = \left( \frac{\partial S}{\partial x} \right)_y \, dx + \left( \frac{\partial S}{\partial y} \right)_x \, dy \]

An exact differential
\[
\left( \frac{\partial A}{\partial y} \right)_x = \frac{\partial^2 S}{\partial y \partial x} = \frac{\partial^2 S}{\partial x \partial y} = \left( \frac{\partial B}{\partial x} \right)_y 
\]

⇒ necessary condition, but it is also sufficient

Exact differential if and only if
\[
\left( \frac{\partial A}{\partial y} \right)_x = \left( \frac{\partial B}{\partial x} \right)_y
\]

Then \(\int_1^2 dS = S(x_2, y_2) - S(x_1, y_1)\) is independent of the path.
III) Integrating an exact differential

\[ dS = A(x, y) \, dx + B(x, y) \, dy \]

1. Integrate a coefficient with respect to one variable

\[ \left( \frac{\partial S}{\partial x} \right)_y = A(x, y) \]

\[ S(x, y) = \int A(x, y) \, dx + f(y) \]

\[ y \text{ fixed} \]
2. Differentiate result with respect to other variable

\[
\left( \frac{\partial S}{\partial y} \right)_x = \frac{\partial}{\partial y} \left[ \int A(x, y) \, dx \right] + \frac{d f(y)}{dy} = B(x, y)
\]

3. Integrate again to find \( f(y) \)

\[
\frac{d f(y)}{dy} = \left\{ B(x, y) - \frac{\partial}{\partial y} \int A(x, y) \, dx \right\}
\]

\[
f(y) = \int \{ \cdots \} \, dy
\]

done