

From thermodynamics to geodynamics: An overview of the geophysical thermodynamics of phase relations

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Thermodynamics ↔ Geodynamics

We will explore thermodynamic fundamentals behind various geophysical and geodynamical processes, drawing upon a subset of the following topics:

- Equilibrium, the phase rule, chemical potentials, and the lever rule
 - Clapeyron slopes, exothermic and endothermic reactions, dehydration
 - Geobarometry and geothermometry
 - Reactions: gabbro $\rightarrow$ eclogite; plagioclase $\rightarrow$ spinel $\rightarrow$ garnet lherzolite
 - Role of garnet: eclogite $\rightarrow$ garnetite; garnet $\rightarrow$ silicate perovskite
 - Cation-exchange coupling: α - β -garnet; γ -pv-mw-gt
 - Temperature-dependent transitions: $(\text{Mg,Fe})_2\text{SiO}_4$ olivine; silicate ilmenite
 - Phase destabilization: oxide transitions
 - Thermoelastic equations of state: correlated uncertainty; lower mantle fitting
 - Dehydration reactions: seismicity and volcanism
 - Metastability: seismic signatures, anomalous latent heat release
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- seismic velocity discontinuities and gradients
 - mantle convection
 - lithospheric subsidence
 - subduction zone processes

Welcome

You are welcome to interrupt and ask questions!

Some discussion will make these lectures more interesting.

Unfortunately, I do not know everyone's background in thermodynamics. So, I will spend the first lecture reviewing some of the fundamentals. This part will be rather mathematical (primarily following the approach of Callen [1960, 1985]), and probably we will not begin to discuss interesting geological and geophysical examples until the next lectures.

After each lecture, I will post some notes (PDF) at:

<http://ajisai.earth.northwestern.edu/private/karel2011/>

An Apology

Many of the figures I have used to illustrate these various ideas are drawn from my own work or from that of my colleagues. This is simply because I have convenient access to these particular figures. Many other scientists have contributed far more to the study of most of these topics. I offer my apologies for not having used more of their figures instead.

What is Thermodynamics?

A Quick Review of Fundamentals...

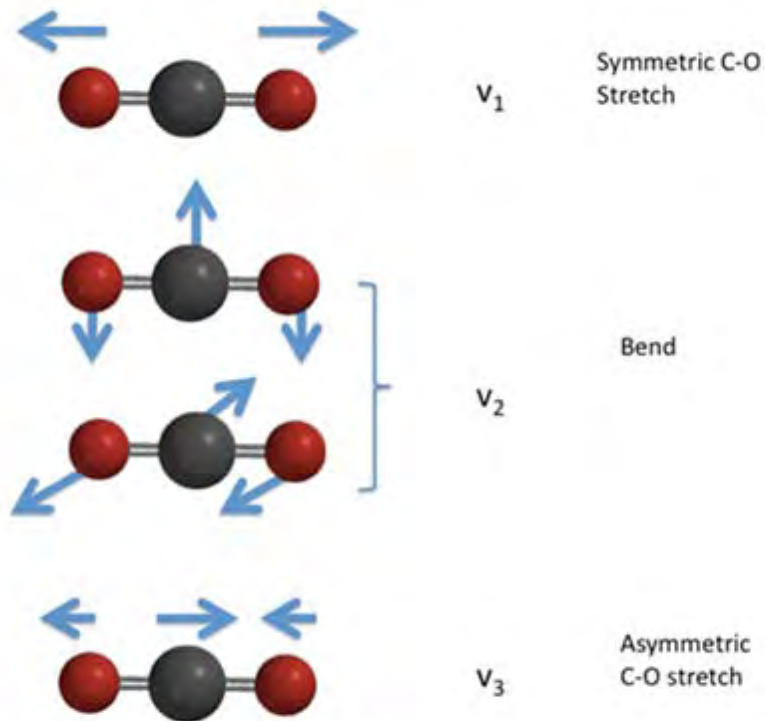


Fig. 1 Vibrational modes of CO₂

(Lin and Lu, 2011)

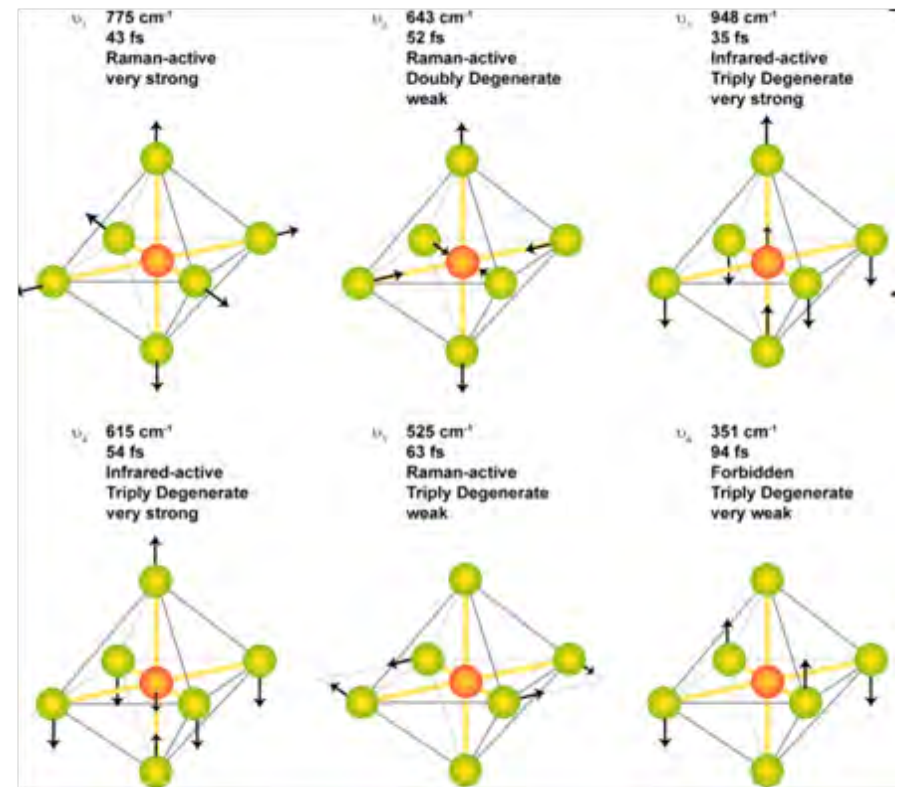


Fig. 4 Normal modes of vibrations for SF₆

(Wagner et al., 2006)

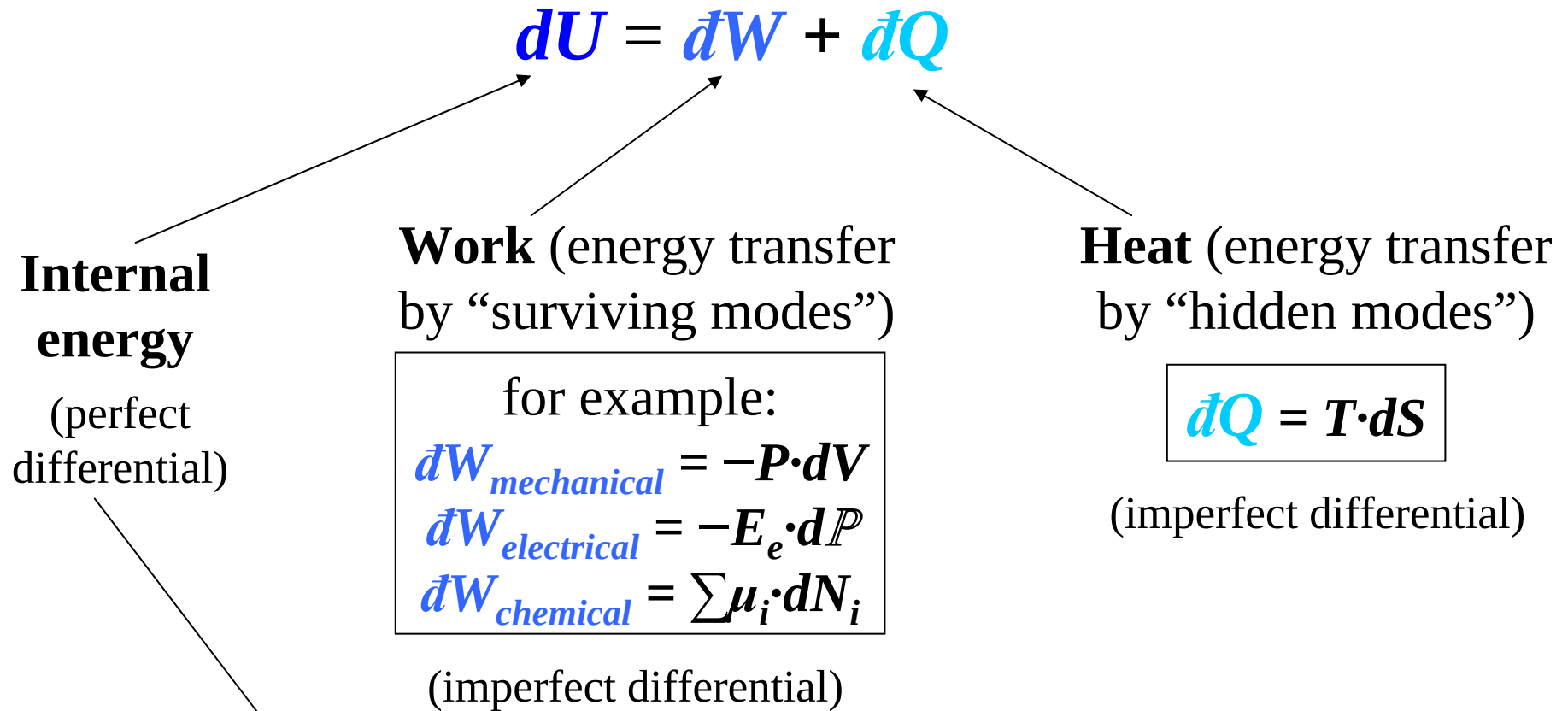
Thermodynamics and normal modes of atomic oscillation

“Of the enormous number of atomic coordinates, a very few, with unique symmetry properties, survive the statistical averaging associated with a transition to a macroscopic description. Certain of these surviving coordinates are mechanical in nature – they are volume, parameters descriptive of the shape (components of elastic strain), and the like. Other surviving coordinates are electrical in nature – they are electric dipole moments, magnetic dipole moments, various multipole moments, and the like. *The study of mechanics (including elasticity) is the study of one set of surviving coordinates. The subject of electricity (including electrostatics, magnetostatics, and ferromagnetism) is the study of another set of surviving coordinates.*”

“Thermodynamics, in contrast, is concerned with the macroscopic consequences of the myriads of atomic coordinates that, by virtue of the coarseness of macroscopic observations, do not appear explicitly in a macroscopic description of a system.”

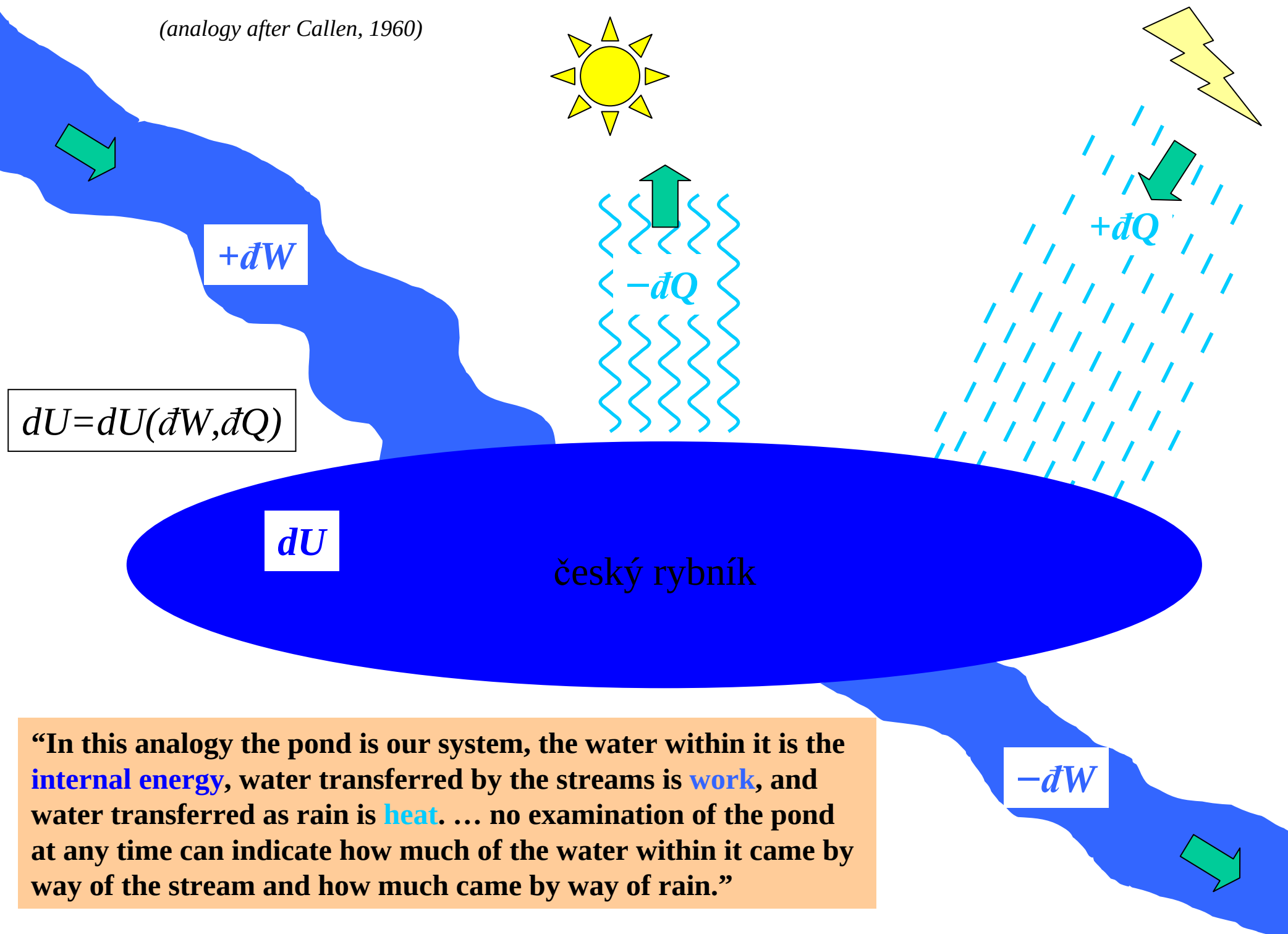
(Callen, 1960)

Energy, Work, and Heat

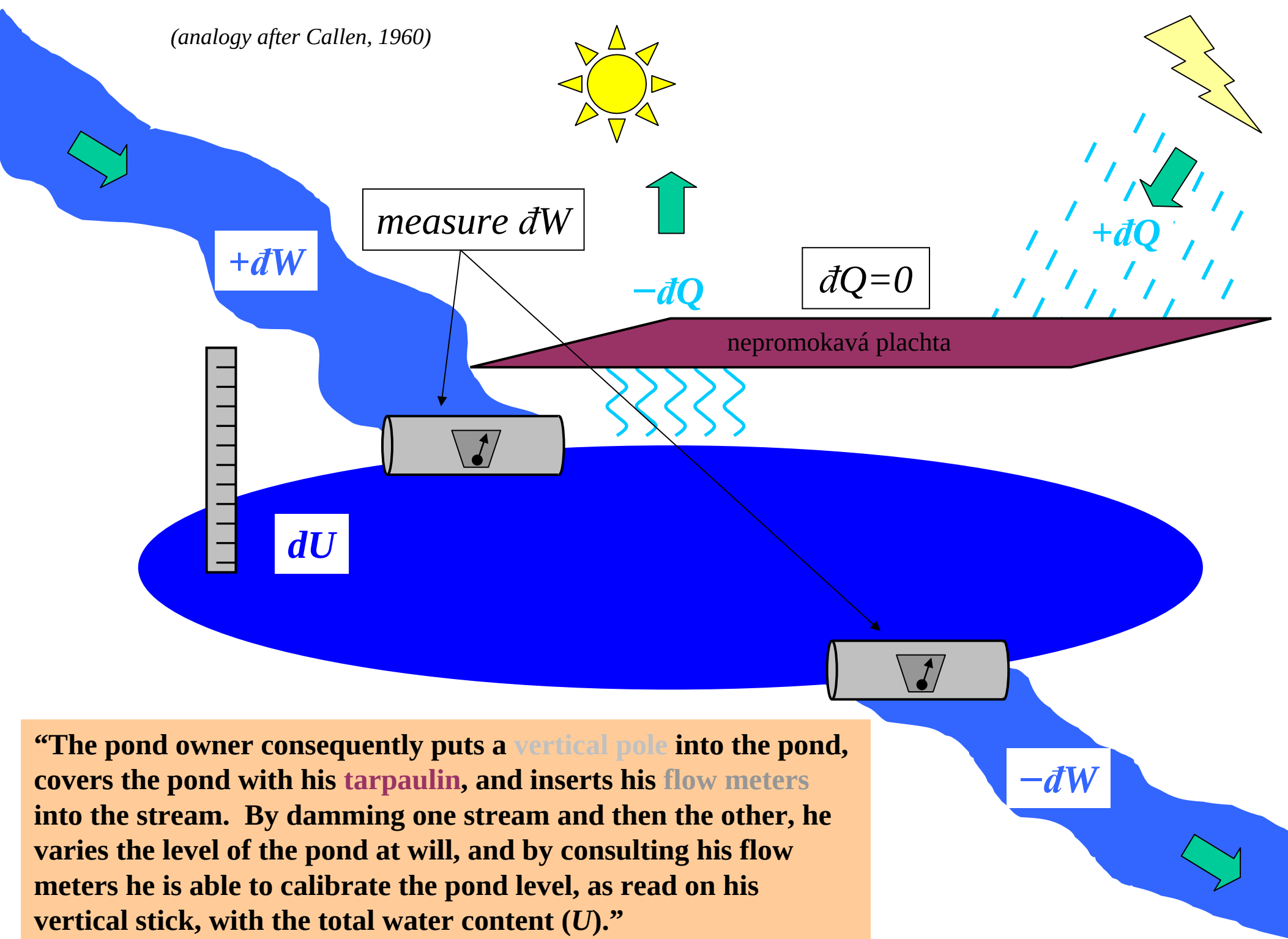


There exists $U = \int dU$ which is a function of the state of the system, but δW and δQ describe energy transfers by particular processes and so cannot be integrated individually to yield state functions.

(analogy after Callen, 1960)

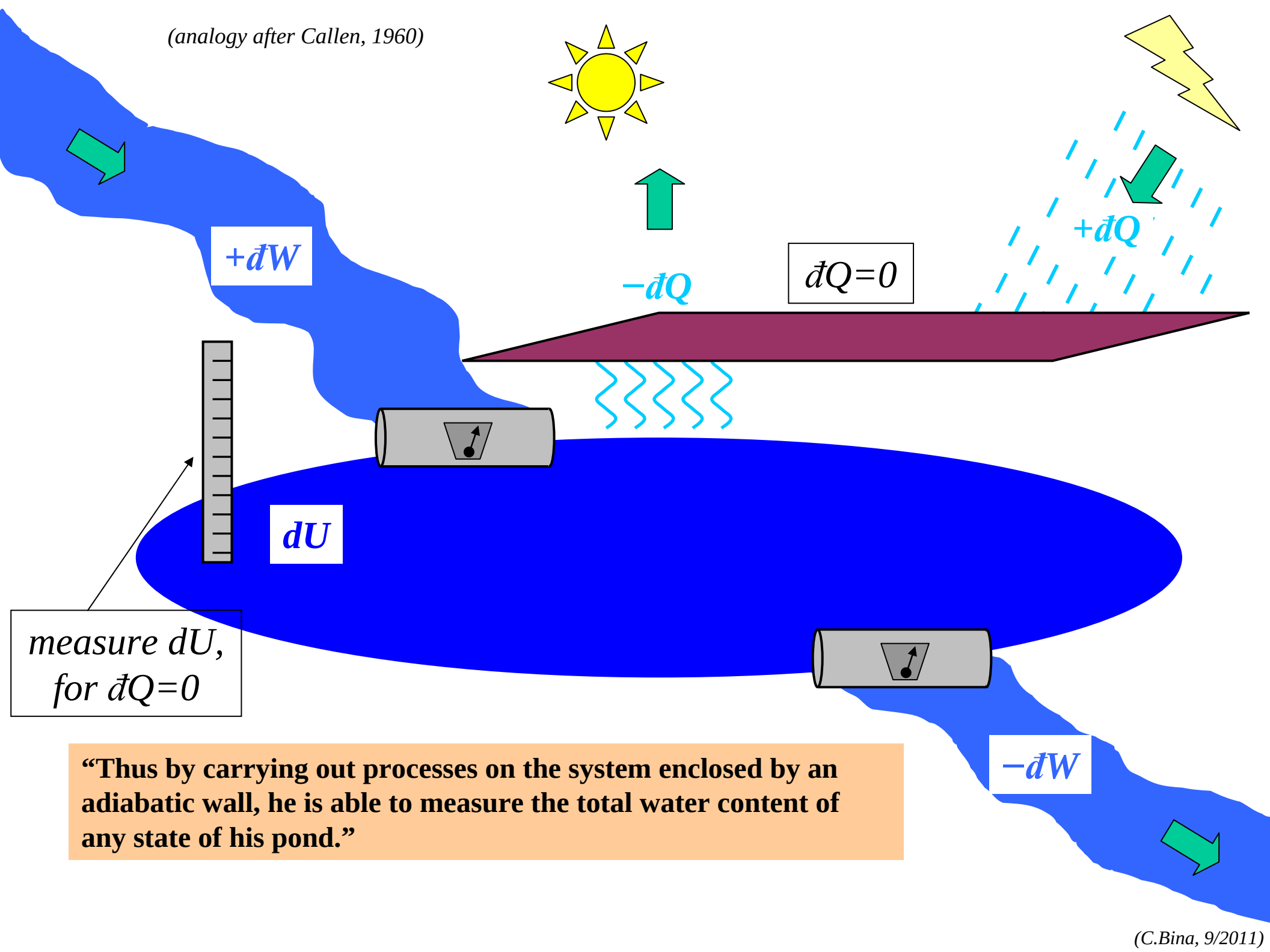


(analogy after Callen, 1960)



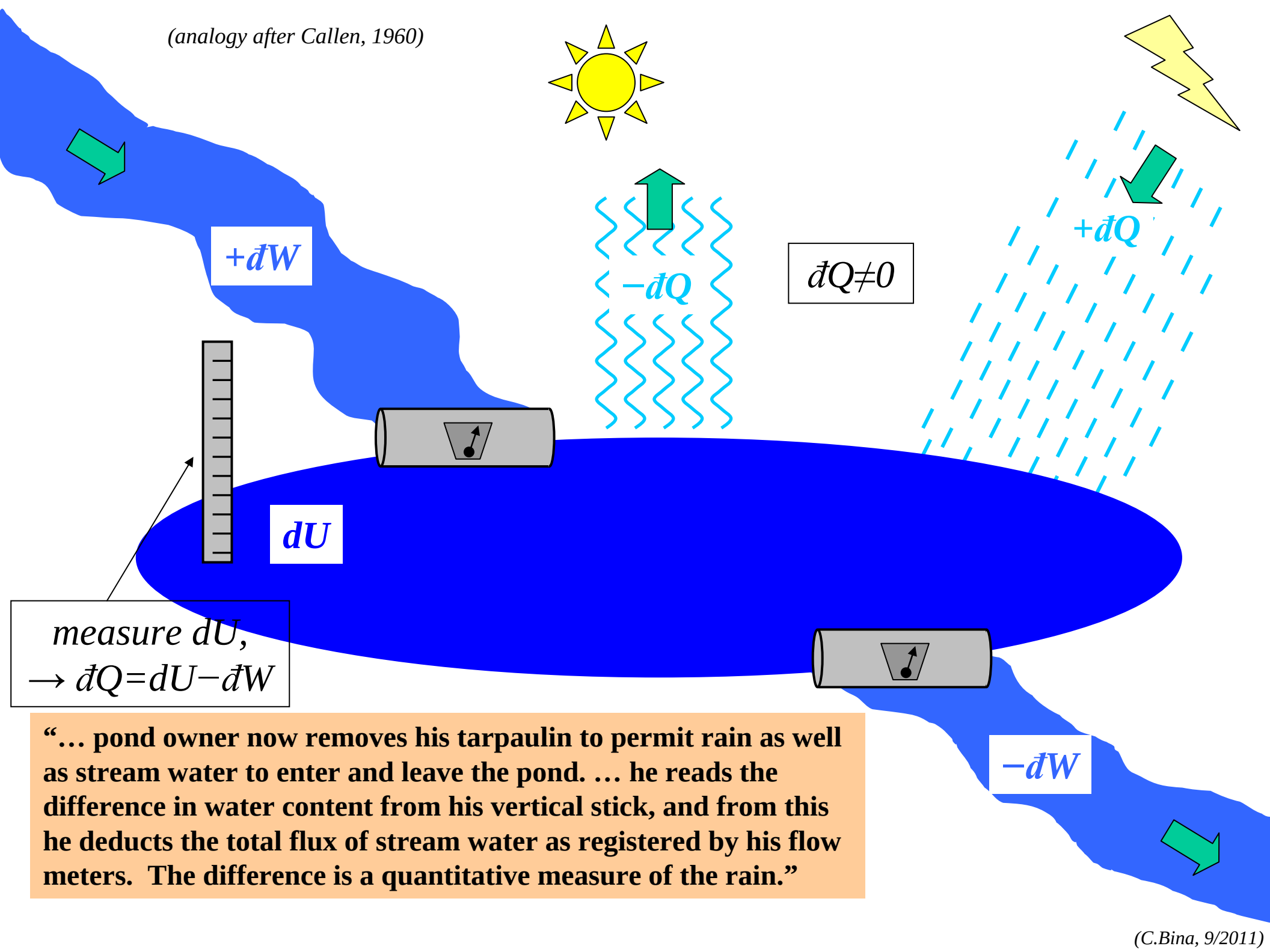
“The pond owner consequently puts a vertical pole into the pond, covers the pond with his tarpaulin, and inserts his flow meters into the stream. By damming one stream and then the other, he varies the level of the pond at will, and by consulting his flow meters he is able to calibrate the pond level, as read on his vertical stick, with the total water content (U).”

(analogy after Callen, 1960)



“Thus by carrying out processes on the system enclosed by an adiabatic wall, he is able to measure the total water content of any state of his pond.”

(analogy after Callen, 1960)



measure dU ,
 $\rightarrow dQ = dU - dW$

“... pond owner now removes his tarpaulin to permit rain as well as stream water to enter and leave the pond. ... he reads the difference in water content from his vertical stick, and from this he deducts the total flux of stream water as registered by his flow meters. The difference is a quantitative measure of the rain.”

$$dU = \delta W + \delta Q$$

There exists $U = \int dU$ which is a function of the state of the system, but δW and δQ describe energy transfers by particular processes and so cannot be integrated individually to yield state functions.

The Basic Problem of Thermodynamics

“The single, all-encompassing problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system.”

(Callen, 1960)

We can approach this problem in various ways. A powerful method is to apply a variational principle to find extrema of a state function – finding conditions, for example, which minimize the internal energy U or which maximize the entropy S . Let us choose first to maximize the entropy S .

Let's invent a function to solve the problem!

We will postulate the existence of a function, called S , that has three or four simple properties which might allow us to solve the problem. Then we will see if the function or its derivatives seem to be related to any of our intuitive ideas of basic physical properties (pressure, temperature, etc.).

“What then is the simplest criterion that reasonably can be imagined for the determination of the final equilibrium state? From our experience with many physical theories we might expect that the most economical form for the equilibrium criterion would be in terms of an extremum principle. That is, we might anticipate the values of the extensive parameters in the final equilibrium state to be simply those that maximize some function. And, straining our optimism to the limit, we might hope that this hypothetical function would have several particularly simple mathematical properties, designed to guarantee simplicity of the derived theory.”

(Callen, 1960)

1. THERMODYNAMIC POSTULATES

- I There exist particular “equilibrium” states that are completely characterized (macroscopically) by the following “extensive” parameters: the internal energy U , the volume V , and the number of moles N_i of each chemical component i :

$$S = S(U, V, \{N_i\}) .$$

an entropy function exists

(1.1)

- II There exists an “entropy” function S of the extensive parameters of any system which is defined for all equilibrium states such that the values assumed by the extensive parameters in the absence of internal constraints are those which maximize the entropy:

$$\text{Equilibrium} \rightarrow dS = 0 , \quad d^2S < 0 .$$

equilibrium maximizes entropy

(1.2)

- III The entropy is a continuous, differentiable, monotonically increasing function of the internal energy, and it is additive over constituent subsystems.

$$\left(\frac{\partial S}{\partial U} \right)_{V, N_i} > 0 , \quad dS = \sum_{\phi} dS^{\phi} .$$

entropy is additive over subsystems

(1.3)

- IV The entropy of any system vanishes in the state of zero temperature:

$$T \equiv \left(\frac{\partial U}{\partial S} \right)_{V, N_i} = 0 \rightarrow S = 0 .$$

(establish zero point of entropy)

(1.4)

2. EQUILIBRIUM IN THE ENTROPY REPRESENTATION

S

Thermodynamic equilibrium is the state, characterized completely by the extensive parameters U (internal energy), V (volume), and N_i (number of moles of component i), in which these parameters, in the absence of internal constraints, assume values which maximize the function S (entropy) for a given value of the total internal energy [cf. Callen, 1960, pp. 43-44]:

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V, N_i} dU + \left(\frac{\partial S}{\partial V} \right)_{U, N_i} dV + \sum_i \left(\frac{\partial S}{\partial N_i} \right)_{U, V, N_j} dN_i = 0. \quad \text{expand } S(U, V, \{N_i\}) \quad (2.1)$$

Upon defining the following “intensive” parameters:

$$P \equiv - \left(\frac{\partial U}{\partial V} \right)_{S, N_i}, \quad T \equiv \left(\frac{\partial U}{\partial S} \right)_{V, N_i}, \quad \mu_i \equiv \left(\frac{\partial U}{\partial N_i} \right)_{S, V, N_j}, \quad \text{name the partial derivatives} \quad (2.2)$$

where P is pressure, T temperature, and μ_i the “chemical potential” of component i , we can express the “entropy maximum principle” (2.1) as:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum_i \frac{\mu_i}{T} dN_i = 0. \quad \text{extremum: } dS=0 \text{ at equilibrium} \quad (2.3)$$

(Strictly, this is an “extremum principle”; the actual “maximum principle” includes an additional $d^2S < 0$ stability requirement [cf. Callen, 1960, pp. 27-28].) Upon considering an internally unconstrained closed system of multiple phases ϕ , equation (2.3) describing thermodynamic equilibrium becomes:

$$dS = \sum_{\phi} dS^{\phi} = \sum_{\phi} \frac{1}{T^{\phi}} dU^{\phi} + \sum_{\phi} \frac{P^{\phi}}{T^{\phi}} dV^{\phi} - \sum_{i, \phi} \frac{\mu_i^{\phi}}{T^{\phi}} dN_i^{\phi} = 0. \quad \sum dS \text{ over subsystems} \quad (2.4)$$

The entropy maximum principle applies to closed systems of fixed volume, bulk composition, and total internal energy, giving the closure conditions:

$$\sum_{\phi} dU^{\phi} = 0, \quad \sum_{\phi} dV^{\phi} = 0, \quad \sum_{\phi} dN_i^{\phi} = 0, \quad \text{for all components } i. \quad \text{closed system} \quad (2.5)$$

(after Callen, 1960)

$$dS = \sum_{\phi} dS^{\phi} = \sum_{\phi} \frac{1}{T^{\phi}} dU^{\phi} + \sum_{\phi} \frac{P^{\phi}}{T^{\phi}} dV^{\phi} - \sum_{i,\phi} \frac{\mu_i^{\phi}}{T^{\phi}} dN_i^{\phi} = 0 . \quad (2.4)$$

The entropy maximum principle applies to closed systems of fixed volume, bulk composition, and total internal energy, giving the closure conditions:

$$\sum_{\phi} dU^{\phi} = 0 , \quad \sum_{\phi} dV^{\phi} = 0 , \quad \sum_{\phi} dN_i^{\phi} = 0 , \quad \text{for all components } i . \quad \boxed{\text{closed system}} \quad (2.5)$$

Upon solving equation (2.4) subject to equations (2.5), we obtain a description of the equilibrium state. In particular, thermal equilibrium between phases requires uniformity of temperature:

$$\frac{1}{T^{\phi}} = \frac{1}{T^{\psi}} , \quad \text{for all phases } \phi \text{ and } \psi ; \quad \boxed{\text{iso-}T \text{ at equilibrium}} \quad (2.6)$$

mechanical equilibrium between phases requires uniformity of pressure:

$$\frac{P^{\phi}}{T^{\phi}} = \frac{P^{\psi}}{T^{\psi}} , \quad \text{for all phases } \phi \text{ and } \psi ; \quad \boxed{\text{iso-}P \text{ at equilibrium}} \quad (2.7)$$

and mass-transfer equilibrium between phases requires uniformity of chemical potential for each component:

$$\frac{\mu_i^{\phi}}{T^{\phi}} = \frac{\mu_i^{\psi}}{T^{\psi}} , \quad \text{for all components } i \text{ in all phases } \phi \text{ and } \psi . \quad \boxed{\text{iso-}\mu_i \text{ at equilibrium}} \quad (2.8)$$

General thermodynamic equilibrium ($dS = 0$) thus requires simultaneous thermal, mechanical, and mass-transfer equilibrium.

Now let us compare with our intuitive ideas about P and T ...

(after Callen, 1960)

$$dS=0$$

*We found that $T_1=T_2$ at equilibrium,
but how do we get there?*

$$d^2S<0$$

Initially, let $T_1>T_2$.

For a closed system, $dU=dU_1+dU_2=0$.

For $\delta W=0$, we have $dU=TdS$.

So, $dS=dU_1/T_1+dU_2/T_2= dU_1/T_1-dU_1/T_2=0$.

This implies $\Delta S\approx(1/T_1-1/T_2)\Delta U_1$.

For $\Delta S>0$ and $T_1>T_2$, this requires $\Delta U_1 <0$.

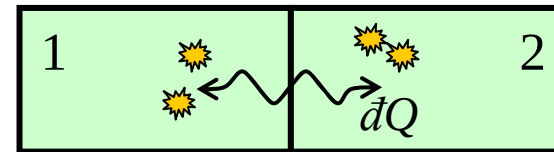
*Thus, heat flows from high-T subsystem 1
to low-T subsystem 2.*

existence: S is extremum

iso-T at equilibrium

stability: S is maximum

*closed system of 2 subsystems:
separated by rigid, immovable,
impermeable, diathermal wall*



*agreement with intuitive concept
of T as temperature*

$$dS=0$$

existence: S is extremum

We found that $P_1=P_2$ at equilibrium,
but how do we get there?

iso- P at equilibrium

$$d^2S < 0$$

stability: S is maximum

Initially, let $P_1 > P_2$.

For the closed system, $dU = dU_1 + dU_2 = 0$,
And for a movable wall $dV = dV_1 + dV_2 = 0$.

For $\delta Q = 0$, we have $dU = -PdV$.

$$\begin{aligned} \text{So, } dS &= (1/T_1 - 1/T_2)dU_1 \\ &+ (P_1/T_1 - P_2/T_2)dV_1/T_1 = 0. \end{aligned}$$

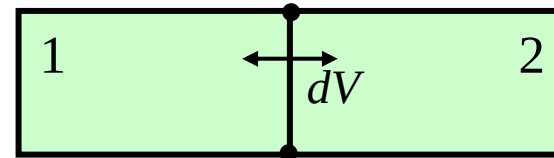
$$\text{For } T_1 = T_2: dS = (P_1/T_1 - P_2/T_1)dV_1 = 0.$$

This implies $\Delta S \approx (P_1/T_1 - P_2/T_1)\Delta V_1$.

For $\Delta S > 0$ and $P_1 > P_2$, this requires $\Delta V_1 > 0$.

Thus, the wall moves so as to increase
volume in high- P subsystem 1 at the expense
of low- P subsystem 2.

closed system of 2 subsystems:
separated by rigid, movable,
impermeable, adiabatic wall



iso- T at equilibrium

agreement with intuitive concept
of P as pressure

$$dS=0$$

existence: S is extremum

We found that $\mu^A_1 = \mu^A_2$ at equilibrium,
but how do we get there?

iso- μ_i at equilibrium

$$d^2S < 0$$

stability: S is maximum

Initially, let $\mu^A_1 > \mu^A_2$.

For the closed system, $dU = dU_1 + dU_2 = 0$;
for A-permeable wall $dN^A = dN^A_1 + dN^A_2 = 0$.

For $\delta Q = 0$, we have $dU = -PdV$.

$$\begin{aligned} \text{So, } dS &= (1/T_1 - 1/T_2)dU_1 \\ &\quad - (\mu^A_1/T_1 - \mu^A_2/T_2)dN^A_1 = 0. \end{aligned}$$

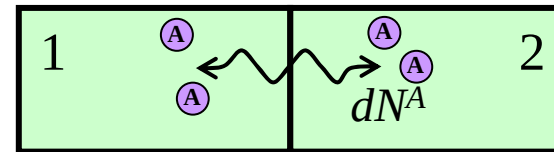
$$\text{For } T_1 = T_2: dS = -(\mu^A_1/T_1 - \mu^A_2/T_1)dN^A_1 = 0.$$

This implies $\Delta S \approx -(\mu^A_1/T_1 - \mu^A_2/T_1)\Delta N^A_1$.

For $\Delta S > 0$ and $\mu^A_1 > \mu^A_2$, we have $\Delta N^A_1 < 0$.

Thus, species A moves from high- μ^A
subsystem 1 to low- μ^A subsystem 2.

closed system of 2 subsystems:
separated by rigid, immovable,
A-permeable, adiabatic wall



iso- T at equilibrium

suggests μ^i is related to intuitive
concept of concentration

(after Callen, 1960)

3. EQUILIBRIUM IN THE ENERGY REPRESENTATION

$$U \leftrightarrow S$$

Moving from the entropy representation $S(U, V, \{N_i\})$ to the energy representation $U(S, V, \{N_i\})$, we obtain an equivalent statement [cf. Callen, 1960, pp. 86-88]. Thermodynamic equilibrium is the state, characterized completely by the extensive parameters S (entropy), V (volume), and N_i (number of moles of component i), in which these parameters, in the absence of internal constraints, assume values which minimize the function U (internal energy) for a given value of the total entropy [cf. Callen, 1960, p. 88]:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_i} dV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_j} dN_i = 0. \quad \text{expand } U(S, V, \{N_i\}) \quad (3.1)$$

Upon employing the definitions of the intensive parameters:

$$P \equiv -\left(\frac{\partial U}{\partial V}\right)_{S, N_i}, \quad T \equiv \left(\frac{\partial U}{\partial S}\right)_{V, N_i}, \quad \mu_i \equiv \left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_j}, \quad \text{name the partial derivatives} \quad (3.2)$$

where P is pressure, T temperature, and μ_i the “chemical potential” of component i , we can express the “energy minimum principle” (3.1) as:

$$dU = TdS - PdV + \sum_i \mu_i dN_i = 0. \quad \text{extremum: } dU=0 \text{ at equilibrium} \quad (3.3)$$

(Strictly, this is an “extremum principle”; the actual “minimum principle” includes an additional $d^2U > 0$ stability requirement [cf. Callen, 1960, pp. 27-28].) Upon considering an internally unconstrained closed system of multiple phases ϕ , equation (3.3) describing thermodynamic equilibrium becomes:

$$dU = \sum_{\phi} dU^{\phi} = \sum_{\phi} T^{\phi} dS^{\phi} - \sum_{\phi} P^{\phi} dV^{\phi} + \sum_{i, \phi} \mu_i^{\phi} dN_i^{\phi} = 0. \quad \sum dU \text{ over subsystems} \quad (3.4)$$

The energy minimum principle applies to closed systems of fixed volume, bulk composition, and total entropy, giving the closure conditions:

$$\sum_{\phi} dS^{\phi} = 0, \quad \sum_{\phi} dV^{\phi} = 0, \quad \sum_{\phi} dN_i^{\phi} = 0, \quad \text{for all components } i \quad \text{closed system} \quad (3.5)$$

(cf. Bina and Kumazawa, 1993)

(C.Bina, 9/2011)

(after Callen, 1960)

$$dU = \sum_{\phi} dU^{\phi} = \sum_{\phi} T^{\phi} dS^{\phi} - \sum_{\phi} P^{\phi} dV^{\phi} + \sum_{i,\phi} \mu_i^{\phi} dN_i^{\phi} = 0 . \quad (3.4)$$

The energy minimum principle applies to closed systems of fixed volume, bulk composition, and total entropy, giving the closure conditions:

$$\sum_{\phi} dS^{\phi} = 0 , \quad \sum_{\phi} dV^{\phi} = 0 , \quad \sum_{\phi} dN_i^{\phi} = 0 , \quad \text{for all components } i . \quad \boxed{\text{closed system}} \quad (3.5)$$

Upon solving equation (3.4) subject to equations (3.5), we obtain the standard description of the equilibrium state. In particular, thermal equilibrium between phases requires uniformity of temperature:

$$T^{\phi} = T^{\psi} , \quad \text{for all phases } \phi \text{ and } \psi ; \quad \boxed{\text{iso-}T \text{ at equilibrium}} \quad (3.6)$$

mechanical equilibrium between phases requires uniformity of pressure:

$$P^{\phi} = P^{\psi} , \quad \text{for all phases } \phi \text{ and } \psi ; \quad \boxed{\text{iso-}P \text{ at equilibrium}} \quad (3.7)$$

and mass-transfer equilibrium between phases requires uniformity of chemical potential for each component:

$$\mu_i^{\phi} = \mu_i^{\psi} , \quad \text{for all components } i \text{ in all phases } \phi \text{ and } \psi . \quad \boxed{\text{iso-}\mu_i \text{ at equilibrium}} \quad (3.8)$$

General thermodynamic equilibrium ($dU = 0$) thus requires simultaneous thermal, mechanical, and mass-transfer equilibrium.

In both the entropy and energy representations, the independent variables are all extensive parameters. We may replace some of these independent variables with intensive parameters through the technique of partial Legendre transformation [cf. Callen, 1960, pp. 90-98], yielding the “enthalpy” H , “Helmholtz” F , and “Gibbs” G thermodynamic potentials, for example (Table A1). Since P and T are the variables most easily controlled in the laboratory environment, we shall usually employ the Gibbs potential G . This formalism results in three “equations of state” in terms of our chosen independent variables:

$$S = S(T, P, \{N_i\}) , \quad V = V(T, P, \{N_i\}) , \quad \mu_i = \mu_i(T, P, \{N_i\}) . \quad \boxed{\text{equations of state}}$$

(cf. Bina and Kumazawa, 1993)

(C.Bina, 9/2011)

TABLE A1. Summary of some common thermodynamic potentials.

<u>Entropy: $S = S(U, V, \{N_i\})$</u> $dS = \left(\frac{\partial S}{\partial U}\right)_{V, \{N_i\}} dU + \left(\frac{\partial S}{\partial V}\right)_{U, \{N_i\}} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{U, V, \{N_{j \neq i}\}} dN_i = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV - \sum_i \left(\frac{\mu_i}{T}\right) dN_i$ $S = \left(\frac{1}{T}\right) U + \left(\frac{P}{T}\right) V - \sum_i \left(\frac{\mu_i}{T}\right) N_i, \quad 0 = U d\left(\frac{1}{T}\right) + V d\left(\frac{P}{T}\right) - \sum_i N_i d\left(\frac{\mu_i}{T}\right)$ $T = T(U, V, \{N_i\}), \quad P = P(U, V, \{N_i\}), \quad \mu_i = \mu_i(U, V, \{N_i\})$ Equilibrium maximizes S at constant U.
<u>Internal Energy: $U = U(S, V, \{N_i\})$</u> $dU = \left(\frac{\partial U}{\partial S}\right)_{V, \{N_i\}} dS + \left(\frac{\partial U}{\partial V}\right)_{S, \{N_i\}} dV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S, V, \{N_{j \neq i}\}} dN_i = T dS - P dV + \sum_i \mu_i dN_i$ $U = TS - PV + \sum_i \mu_i N_i, \quad 0 = S dT - V dP + \sum_i N_i d\mu_i$ $T = T(S, V, \{N_i\}), \quad P = P(S, V, \{N_i\}), \quad \mu_i = \mu_i(S, V, \{N_i\})$ Equilibrium minimizes U at constant S.
<u>Helmholtz Potential: $F \equiv U - TS = F(T, V, \{N_i\})$</u> $dF = \left(\frac{\partial F}{\partial T}\right)_{V, \{N_i\}} dT + \left(\frac{\partial F}{\partial V}\right)_{T, \{N_i\}} dV + \sum_i \left(\frac{\partial F}{\partial N_i}\right)_{T, V, \{N_{j \neq i}\}} dN_i = -S dT - P dV + \sum_i \mu_i dN_i$ $F = -PV + \sum_i \mu_i N_i, \quad 0 = S dT - V dP + \sum_i N_i d\mu_i$ $S = S(T, V, \{N_i\}), \quad P = P(T, V, \{N_i\}), \quad \mu_i = \mu_i(T, V, \{N_i\})$ Equilibrium minimizes F at constant T.
<u>Enthalpy: $H \equiv U + PV = H(S, P, \{N_i\})$</u> $dH = \left(\frac{\partial H}{\partial S}\right)_{P, \{N_i\}} dS + \left(\frac{\partial H}{\partial P}\right)_{S, \{N_i\}} dP + \sum_i \left(\frac{\partial H}{\partial N_i}\right)_{S, P, \{N_{j \neq i}\}} dN_i = T dS + V dP + \sum_i \mu_i dN_i$ $H = TS + \sum_i \mu_i N_i, \quad 0 = S dT - V dP + \sum_i N_i d\mu_i$ $T = T(S, P, \{N_i\}), \quad V = V(S, P, \{N_i\}), \quad \mu_i = \mu_i(S, P, \{N_i\})$ Equilibrium minimizes H at constant P.
<u>Gibbs Potential: $G \equiv U - TS + PV = H - TS = G(T, P, \{N_i\})$</u> $dG = \left(\frac{\partial G}{\partial T}\right)_{P, \{N_i\}} dT + \left(\frac{\partial G}{\partial P}\right)_{T, \{N_i\}} dP + \sum_i \left(\frac{\partial G}{\partial N_i}\right)_{T, P, \{N_{j \neq i}\}} dN_i = -S dT + V dP + \sum_i \mu_i dN_i$ $G = \sum_i \mu_i N_i, \quad 0 = S dT - V dP + \sum_i N_i d\mu_i$ $S = S(T, P, \{N_i\}), \quad V = V(T, P, \{N_i\}), \quad \mu_i = \mu_i(T, P, \{N_i\})$ Equilibrium minimizes G at constant P and T.

For each potential: line 1 gives name, definition (if applicable), and fundamental equation; line 2 gives total differential; line 3 gives Euler equation and Gibbs-Duhem relation; line 4 gives three equations of state associated with fundamental equation; line 5 gives equilibrium extremum principle.

A table of some commonly used thermodynamic potentials.

(They are interrelated by various partial Legendre transformations, which exchange dependent and independent variables.)

TABLE A1. Summary of some common thermodynamic potentials.

Entropy: $S = S(U, V, \{N_i\})$ $dS \equiv \left(\frac{\partial S}{\partial U}\right)_{V, \{N_i\}} dU + \left(\frac{\partial S}{\partial V}\right)_{U, \{N_i\}} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{U, V, \{N_{j \neq i}\}} dN_i = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV - \sum_i \left(\frac{\mu_i}{T}\right) dN_i$ $S = \left(\frac{1}{T}\right)U + \left(\frac{P}{T}\right)V - \sum_i \left(\frac{\mu_i}{T}\right)N_i, \quad 0 = U d\left(\frac{1}{T}\right) + V d\left(\frac{P}{T}\right) - \sum_i N_i d\left(\frac{\mu_i}{T}\right)$ $T = T(U, V, \{N_i\}), \quad P = P(U, V, \{N_i\}), \quad \mu_i = \mu_i(U, V, \{N_i\})$ Equilibrium maximizes S at constant U.
Internal Energy: $U = U(S, V, \{N_i\})$ $dU \equiv \left(\frac{\partial U}{\partial S}\right)_{V, \{N_i\}} dS + \left(\frac{\partial U}{\partial V}\right)_{S, \{N_i\}} dV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S, V, \{N_{j \neq i}\}} dN_i = T dS - P dV + \sum_i \mu_i dN_i$ $U = TS - PV + \sum_i \mu_i N_i, \quad 0 = S dT - V dP + \sum_i N_i d\mu_i$ $T = T(S, V, \{N_i\}), \quad P = P(S, V, \{N_i\}), \quad \mu_i = \mu_i(S, V, \{N_i\})$ Equilibrium minimizes U at constant S.

S and U are the two we have just reviewed.

Helmholtz Potential: $F \equiv U - TS = F(T, V, \{N_i\})$ $dF \equiv \left(\frac{\partial F}{\partial T}\right)_{V, \{N_i\}} dT + \left(\frac{\partial F}{\partial V}\right)_{T, \{N_i\}} dV + \sum_i \left(\frac{\partial F}{\partial N_i}\right)_{T, V, \{N_{j \neq i}\}} dN_i = -SdT - PdV + \sum_i \mu_i dN_i$ $F = -PV + \sum_i \mu_i N_i, \quad 0 = SdT - VdP + \sum_i N_i d\mu_i$ $S = S(T, V, \{N_i\}), \quad P = P(T, V, \{N_i\}), \quad \mu_i = \mu_i(T, V, \{N_i\})$ Equilibrium minimizes F at constant T.	
Enthalpy: $H \equiv U + PV = H(S, P, \{N_i\})$ $dH \equiv \left(\frac{\partial H}{\partial S}\right)_{P, \{N_i\}} dS + \left(\frac{\partial H}{\partial P}\right)_{S, \{N_i\}} dP + \sum_i \left(\frac{\partial H}{\partial N_i}\right)_{S, P, \{N_{j \neq i}\}} dN_i = TdS + VdP + \sum_i \mu_i dN_i$ $H = TS + \sum_i \mu_i N_i, \quad 0 = SdT - VdP + \sum_i N_i d\mu_i$ $T = T(S, P, \{N_i\}), \quad V = V(S, P, \{N_i\}), \quad \mu_i = \mu_i(S, P, \{N_i\})$ Equilibrium minimizes H at constant P.	
Gibbs Potential: $G \equiv U - TS + PV = H - TS = G(T, P, \{N_i\})$ $dG \equiv \left(\frac{\partial G}{\partial T}\right)_{P, \{N_i\}} dT + \left(\frac{\partial G}{\partial P}\right)_{T, \{N_i\}} dP + \sum_i \left(\frac{\partial G}{\partial N_i}\right)_{T, P, \{N_{j \neq i}\}} dN_i = -SdT + VdP + \sum_i \mu_i dN_i$ $G = \sum_i \mu_i N_i, \quad 0 = SdT - VdP + \sum_i N_i d\mu_i$ $S = S(T, P, \{N_i\}), \quad V = V(T, P, \{N_i\}), \quad \mu_i = \mu_i(T, P, \{N_i\})$ Equilibrium minimizes G at constant P and T.	G →

For each potential: line 1 gives name, definition (if applicable), and fundamental equation; line 2 gives total differential; line 3 gives Euler equation and Gibbs-Duhem relation; line 4 gives three equations of state associated with fundamental equation; line 5 gives equilibrium extremum principle.

Derivatives of the Gibbs Free Energy: $G(P, T, \{N_i\})$

entropy

$$(\partial G / \partial T)_{P, \{N_j\}} = -S$$

volume

$$(\partial G / \partial P)_{T, \{N_j\}} = V$$

enthalpy

$$\Delta G = \Delta H - T \Delta S$$

chemical potential

$$(\partial G / \partial N_i)_{P, T, (N_{j \neq i})} = \mu_i$$

Gibbs Potential: $G \equiv U - TS + PV = H - TS = G(T, P, \{N_i\})$

$$dG \equiv \left(\frac{\partial G}{\partial T} \right)_{P, \{N_i\}} dT + \left(\frac{\partial G}{\partial P} \right)_{T, \{N_i\}} dP + \sum_i \left(\frac{\partial G}{\partial N_i} \right)_{T, P, \{N_{j \neq i}\}} dN_i = -SdT + VdP + \sum_i \mu_i dN_i$$

$$G = \sum_i \mu_i N_i, \quad 0 = SdT - VdP + \sum_i N_i d\mu_i$$

$$S = S(T, P, \{N_i\}), \quad V = V(T, P, \{N_i\}), \quad \mu_i = \mu_i(T, P, \{N_i\})$$

Equilibrium minimizes G at constant P and T .

For each potential: line 1 gives name, definition (if applicable), and fundamental equation; line 2 gives total differential; line 3 gives Euler equation and Gibbs-Duhem relation; line 4 gives three equations of state associated with fundamental equation; line 5 gives equilibrium extremum principle.

4. THE GIBBS PHASE RULE

Consider a closed multi-phase system of several components, characterized by some uniform pressure P and temperature T . At equilibrium with respect to mass transfer between phases, the chemical potential of each component must be the same in all phases, as indicated in equation (3.8) above. For a system of N components in R phases, we thus have:

$$\mu_i^{\phi_1} = \mu_i^{\phi_2} = \dots = \mu_i^{\phi_R}, \text{ for all components } i, \quad \text{equilibrium} \quad (4.1)$$

giving $R - 1$ equations for each component, or $(R - 1)N$ equations in all. Since the chemical potentials are functions of pressure, temperature, and composition, the unknown quantities in these equations are P , T , and the mole fractions X_i^{ϕ} of each component i in each phase ϕ , given by:

$$X_i^{\phi} \equiv N_i^{\phi} / \sum_i N_i^{\phi}. \quad \text{mole fractions} \quad (4.2)$$

Since $\sum_i X_i^{\phi} = 1$, we have $N - 1$ independent mole fractions for each phase, giving a total of $2 + R(N - 1)$ unknowns.

The number of undetermined variables, or “degrees of freedom” F , is given by the number of unknowns less the number of constraining equations. Hence, we obtain the usual “Gibbs phase rule” [cf. Callen, 1960, pp. 163-167]:

$$F = N + 2 - R. \quad \text{phase rule} \quad (4.3)$$

Thus, for a single-component ($N = 1$) system of Mg_2SiO_4 (forsterite or “Fo”), the number of degrees of freedom F in the equilibrium state is $3 - R$. For one phase ($R = 1$) at equilibrium, we may freely vary two ($F = 2$) parameters (e.g., pressure and temperature). For two phases ($R = 2$) to coexist in equilibrium, we may freely vary one ($F = 1$) parameter (e.g., pressure), but the other (e.g., temperature) will be determined by the equilibrium conditions:

$$\mu_{Fo}^{\alpha}(P, T) = \mu_{Fo}^{\beta}(P, T).$$

phase rule: $N=1$

components:
 $MgO, FeO,$
 $SiO_2, \text{ etc.}$

phases:
 $olv-(Mg,Fe)_2SiO_4,$
 $opx-(Mg,Fe)SiO_3, \text{ etc.}$

$2 + R(N - 1)$ Unknowns:

$$\left\{ \begin{array}{l} P, T \\ X_1^{\phi_1}, X_2^{\phi_1}, \dots, X_{N-1}^{\phi_1} \\ X_1^{\phi_2}, X_2^{\phi_2}, \dots, X_{N-1}^{\phi_2} \\ \dots \\ X_1^{\phi_R}, X_2^{\phi_R}, \dots, X_{N-1}^{\phi_R} . \end{array} \right.$$

*derivation of the
phase rule*

$(R - 1)N$ Equations:

$$\left\{ \begin{array}{l} \mu_1^{\phi_1} = \mu_1^{\phi_2} = \dots = \mu_1^{\phi_R} \\ \mu_2^{\phi_1} = \mu_2^{\phi_2} = \dots = \mu_2^{\phi_R} \\ \dots \\ \mu_N^{\phi_1} = \mu_N^{\phi_2} = \dots = \mu_N^{\phi_R} . \end{array} \right.$$

Degrees of Freedom:

$$F = [2 + R(N - 1)] - [(R - 1)N] = N + 2 - R .$$

$$F = N + 2 - R$$

THE PHASE RULE

$$N=1$$

Degrees of Freedom = 2 [P,T] + Components – Phases
 $F = 2 + N - R$

One Component ($Fo = \text{Mg}_2\text{SiO}_4$):

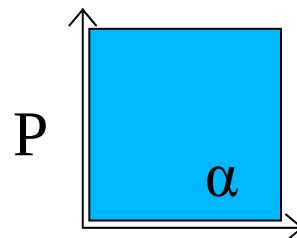
$$N = 1 \rightarrow F = 2 + 1 - R = 3 - R$$

One Phase (α): (α =olivine)

$$\mu_{Fo}^{\alpha}(P, T)$$

$$R = 1 \rightarrow F = 2 \text{ (divariant)}$$

$$N=1, R=1: F=2$$

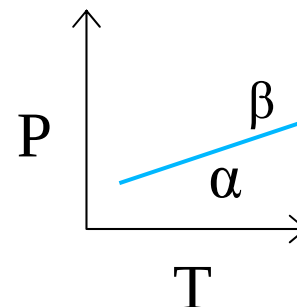


Two Phases (α and β): (β =wadsleyite)

$$\mu_{Fo}^{\alpha}(P, T) = \mu_{Fo}^{\beta}(P, T)$$

$$R = 2 \rightarrow F = 1 \text{ (univariant)}$$

$$N=1, R=2: F=1$$

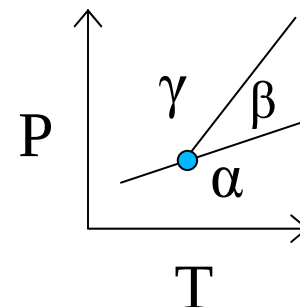


Three Phases (α , β , and γ): (γ =ringwoodite)

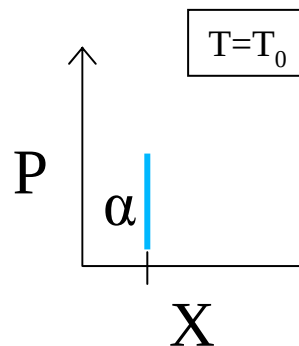
$$\mu_{Fo}^{\alpha}(P, T) = \mu_{Fo}^{\beta}(P, T) = \mu_{Fo}^{\gamma}(P, T)$$

$$R = 3 \rightarrow F = 0 \text{ (invariant)}$$

$$N=1, R=3: F=0$$



$$N=1, R=1: F'=1$$

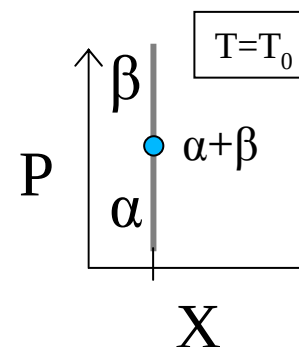


Fix T at constant T_0 : $F' = F - 1$

$$R = 1 \rightarrow F' = 1$$

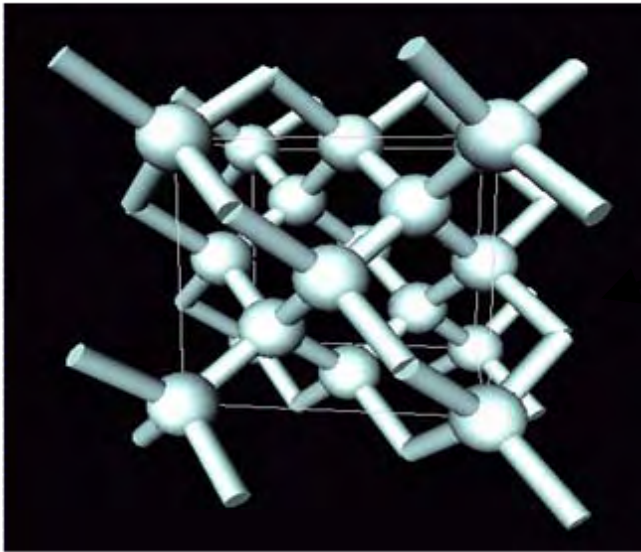
$$R = 2 \rightarrow F' = 0$$

$$N=1, R=2: F'=0$$

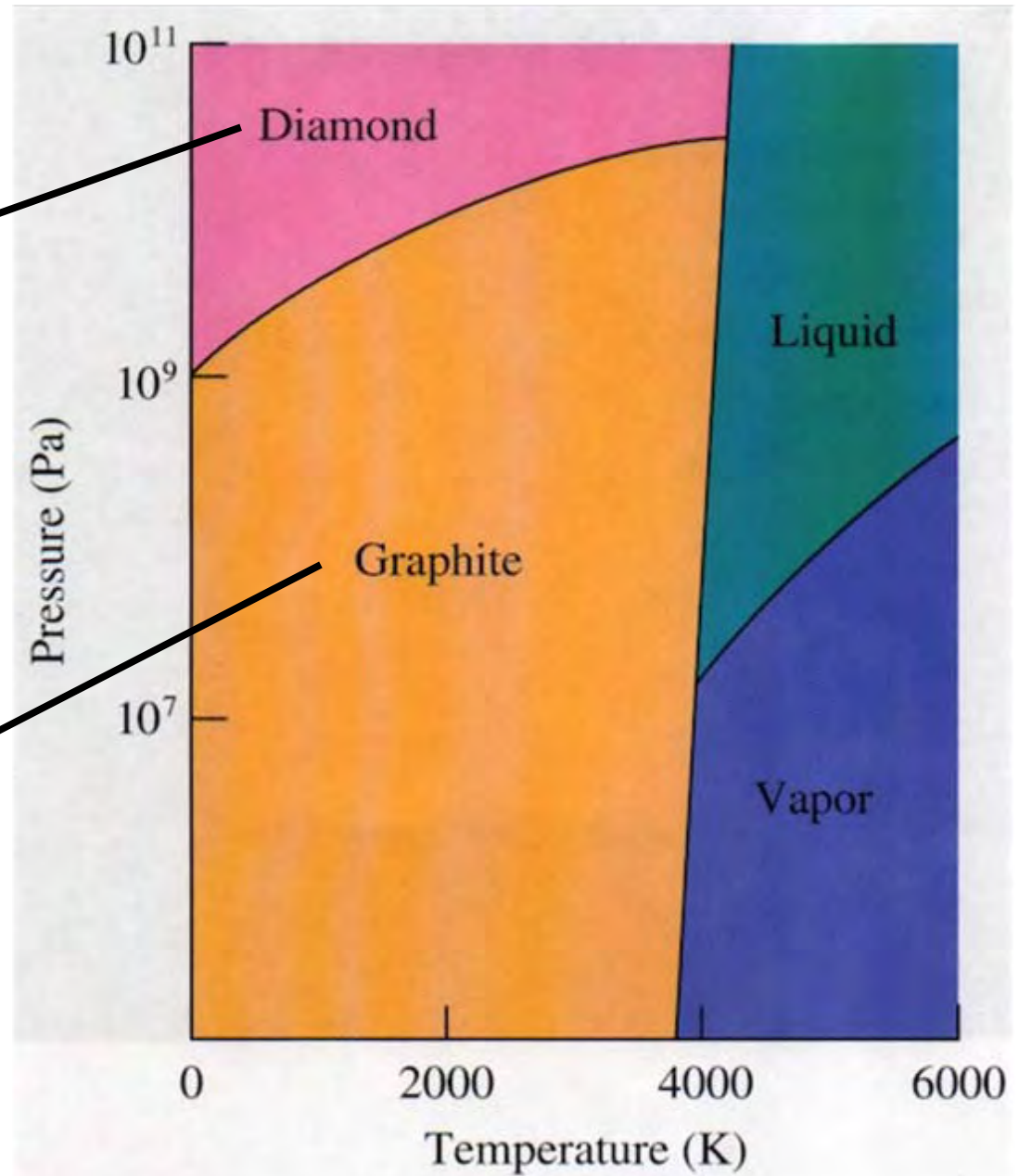


Phase Transitions in Carbon

$N=1$



(structures from Hewat [1998])



(diagram by A. Sayfa, after Bundy [1989])

Thus, for a single-component ($N = 1$) system of Mg_2SiO_4 (forsterite or “Fo”), the number of degrees of freedom F in the equilibrium state is $3 - R$. For one phase ($R = 1$) at equilibrium, we may freely vary two ($F = 2$) parameters (*e.g.*, pressure and temperature). For two phases ($R = 2$) to coexist in equilibrium, we may freely vary one ($F = 1$) parameter (*e.g.*, pressure), but the other (*e.g.*, temperature) will be determined by the equilibrium conditions:

$$\mu_{Fo}^{\alpha}(P, T) = \mu_{Fo}^{\beta}(P, T) .$$

phase rule: $N=1$

The P - T or “Clapeyron” slope, $dP/dT = \Delta S/\Delta V$, gives the slope at any point along the the boundary curve between the two coexisting phases. For three phases ($R = 3$) to coexist in equilibrium, we may freely vary no ($F = 0$) parameters; all parameters (*e.g.*, temperature and pressure) will be determined by the equilibrium conditions.

Furthermore, for a two-component ($N = 2$) system of Mg_2SiO_4 (forsterite or “Fo”) and Fe_2SiO_4 (fayalite or “Fa”), the number of degrees of freedom F in the equilibrium state is $4 - R$. For one phase ($R = 1$) at equilibrium, we may freely vary three ($F = 3$) parameters (*e.g.*, pressure, temperature, and composition of the phase). For two phases ($R = 2$) to coexist in equilibrium, we may freely vary two ($F = 2$) parameters (*e.g.*, pressure and temperature), but the others (*e.g.*, the compositions of the two phases) will be determined by the equilibrium conditions:

$$\mu_{Fo}^{\alpha}(P, T, X_{Fo}^{\alpha}) = \mu_{Fo}^{\beta}(P, T, X_{Fo}^{\beta})$$

$$\mu_{Fa}^{\alpha}(P, T, X_{Fa}^{\alpha}) = \mu_{Fa}^{\beta}(P, T, X_{Fa}^{\beta}) .$$

phase rule: $N=2$

For three phases ($R = 3$) to coexist in equilibrium, we may freely vary one ($F = 1$) parameter (*e.g.*, temperature), but the others (*e.g.*, pressure and the compositions of the three phases) will be determined by the equilibrium conditions.

phase rule: $N=3$

THE PHASE RULE

$$N=2$$

Degrees of Freedom = 2 [P,T] + Components – Phases

$$F = 2 + N - R$$

Two Components ($F_o = \text{Mg}_2\text{SiO}_4$ and $F_a = \text{Fe}_2\text{SiO}_4$):

$$N = 2 \rightarrow F = 2 + 2 - R = 4 - R$$

One Phase (α): (α =olivine)

$$\mu_{F_o}^{\alpha}(P, T, X_{F_o}^{\alpha})$$

$$\mu_{F_a}^{\alpha}(P, T, X_{F_o}^{\alpha})$$

[Note: $X_{F_o}^{\alpha} = 1 - X_{F_a}^{\alpha}$]

$$R = 1 \rightarrow F = 3 \text{ (trivariant)}$$

Two Phases (α and β): (β =wadsleyite)

$$\mu_{F_o}^{\alpha}(P, T, X_{F_o}^{\alpha}) = \mu_{F_o}^{\beta}(P, T, X_{F_o}^{\beta})$$

$$\mu_{F_a}^{\alpha}(P, T, X_{F_o}^{\alpha}) = \mu_{F_a}^{\beta}(P, T, X_{F_o}^{\beta})$$

$$R = 2 \rightarrow F = 2 \text{ (divariant)}$$

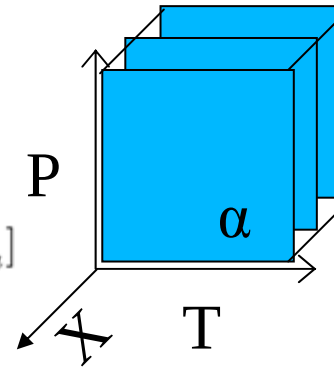
Three Phases (α , β , and γ): (γ =ringwoodite)

$$\mu_{F_o}^{\alpha}(P, T, X_{F_o}^{\alpha}) = \mu_{F_o}^{\beta}(P, T, X_{F_o}^{\beta}) = \mu_{F_o}^{\gamma}(P, T, X_{F_o}^{\gamma})$$

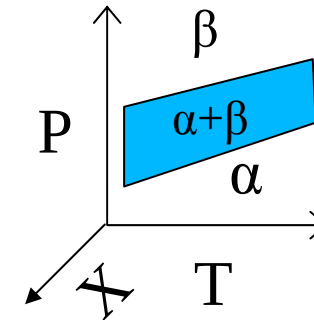
$$\mu_{F_a}^{\alpha}(P, T, X_{F_o}^{\alpha}) = \mu_{F_a}^{\beta}(P, T, X_{F_o}^{\beta}) = \mu_{F_a}^{\gamma}(P, T, X_{F_o}^{\gamma})$$

$$R = 3 \rightarrow F = 1 \text{ (univariant)}$$

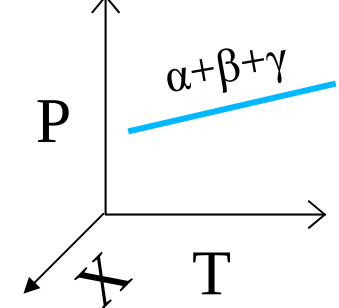
$$N=2, R=1: F=3$$



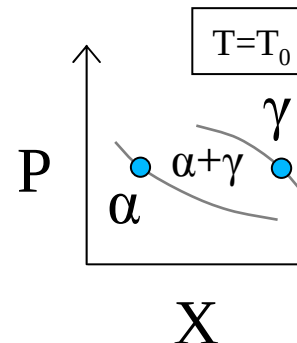
$$N=2, R=2: F=2$$



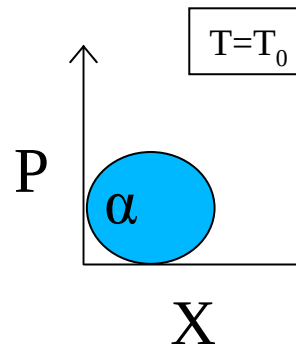
$$N=2, R=3: F=1$$



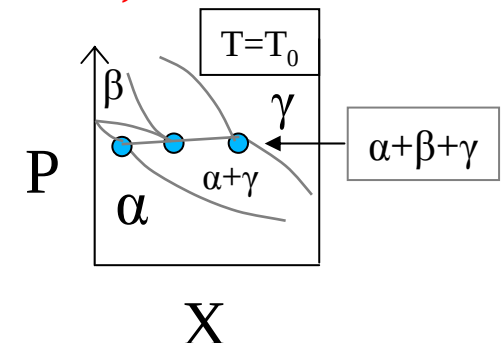
$$N=2, R=2: F'=1$$



$$N=2, R=1: F'=2$$



$$N=2, R=3: F'=0$$



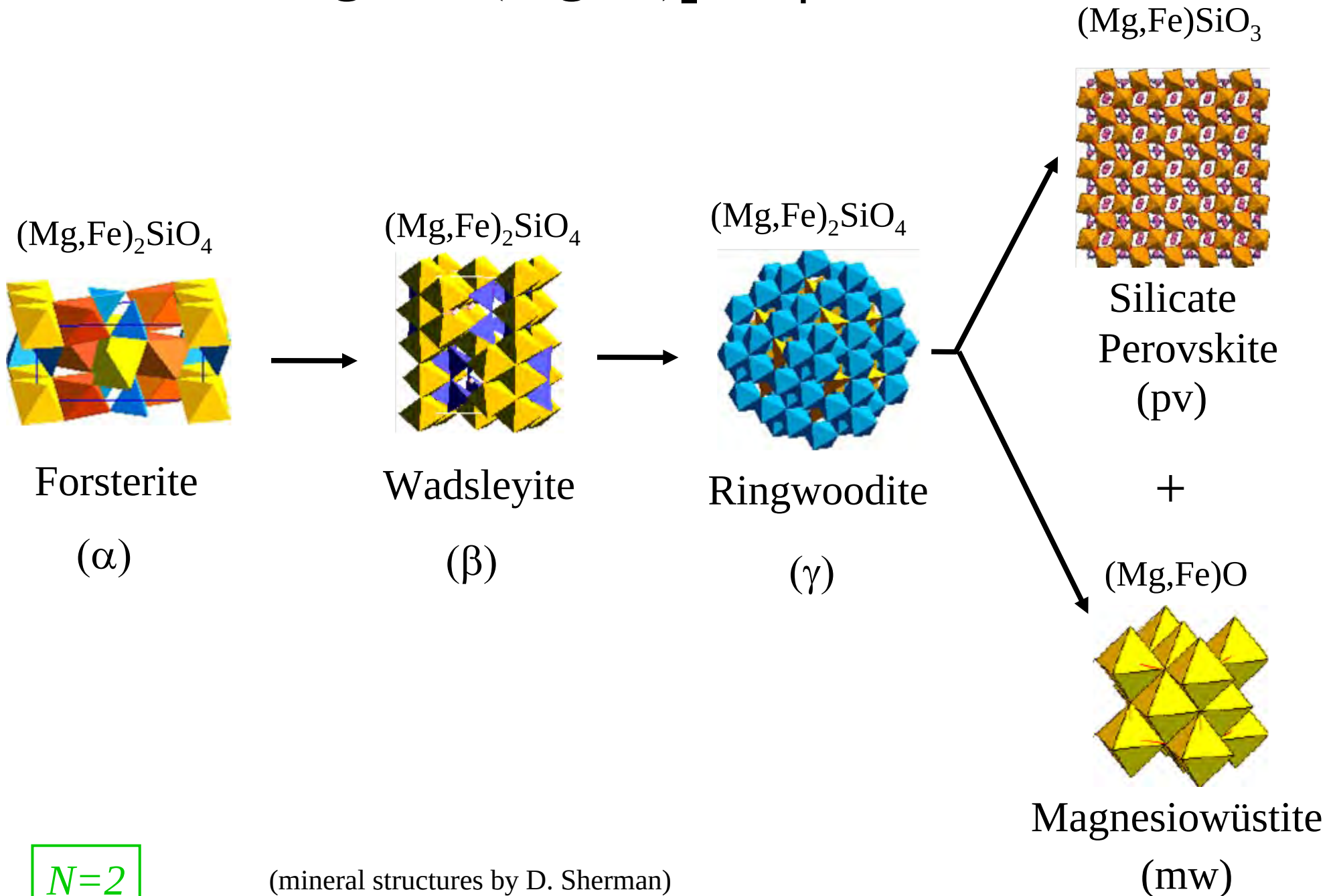
Fix T at constant T_0 : $F' = F - 1$

$$R = 1 \rightarrow F' = 2$$

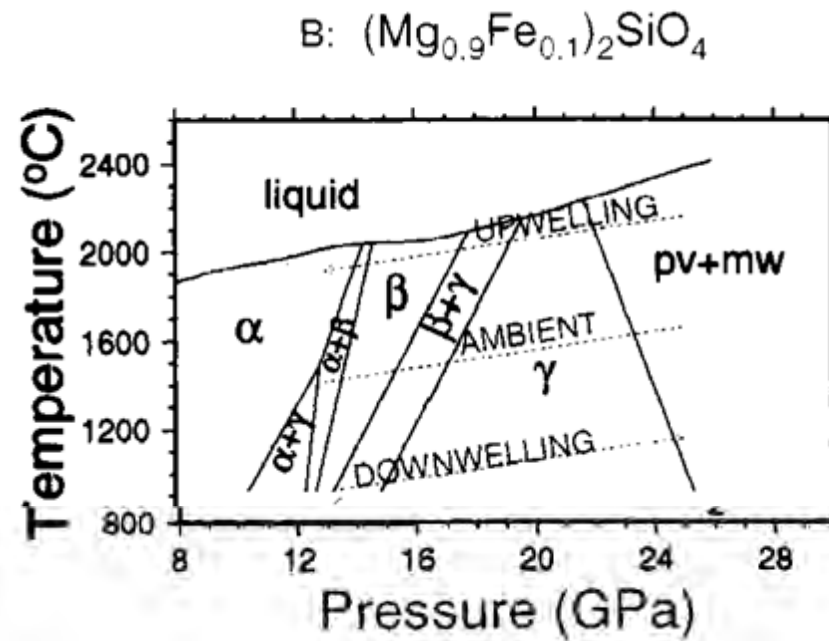
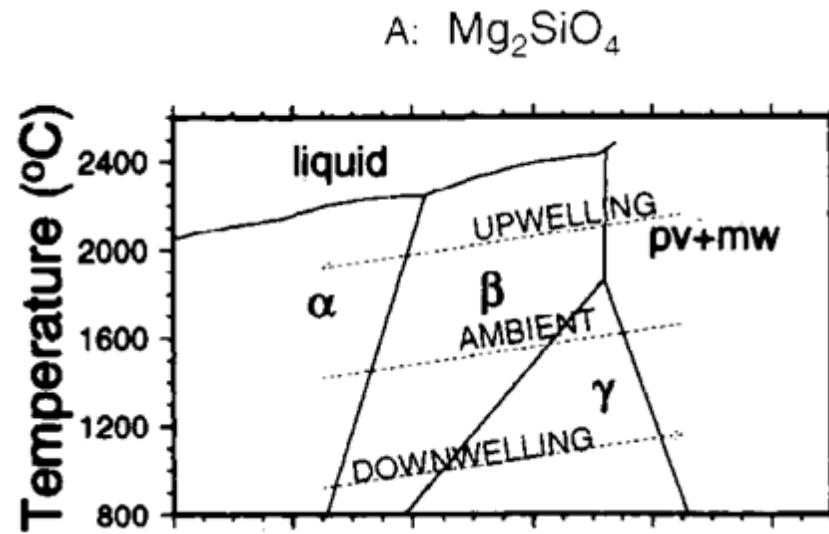
$$R = 2 \rightarrow F' = 1$$

$$R = 3 \rightarrow F' = 0$$

Phase Changes in $(\text{Mg,Fe})_2\text{SiO}_4$ Olivine



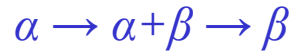
$N=1$



$N=2$

(from Figure 1 of Bina and Liu, 1995)

Equilibrium Olivine Phase Relations



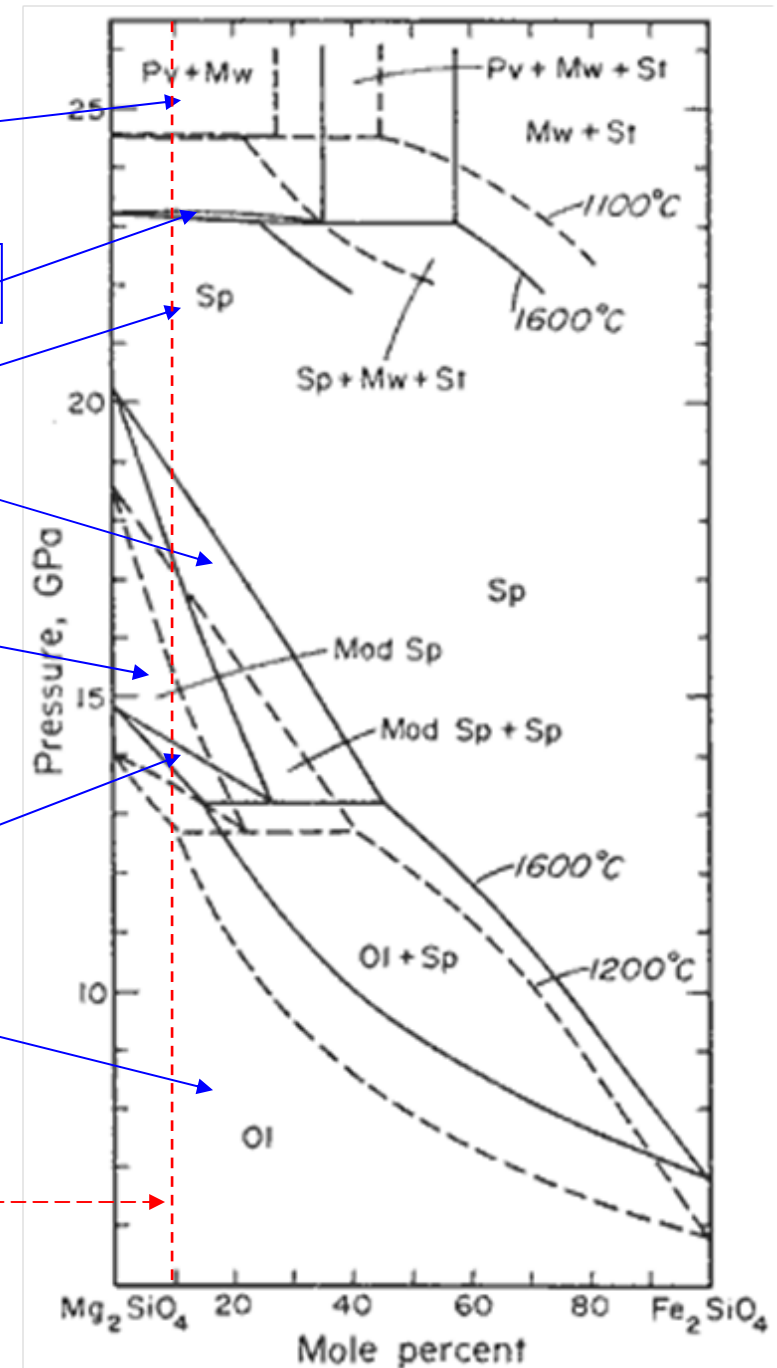
$\alpha = \text{Ol}$
 $\beta = \text{Mod Sp}$
 $\gamma = \text{Sp}$

$N=2$

660 km discontinuity

410 km discontinuity

mantle $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$

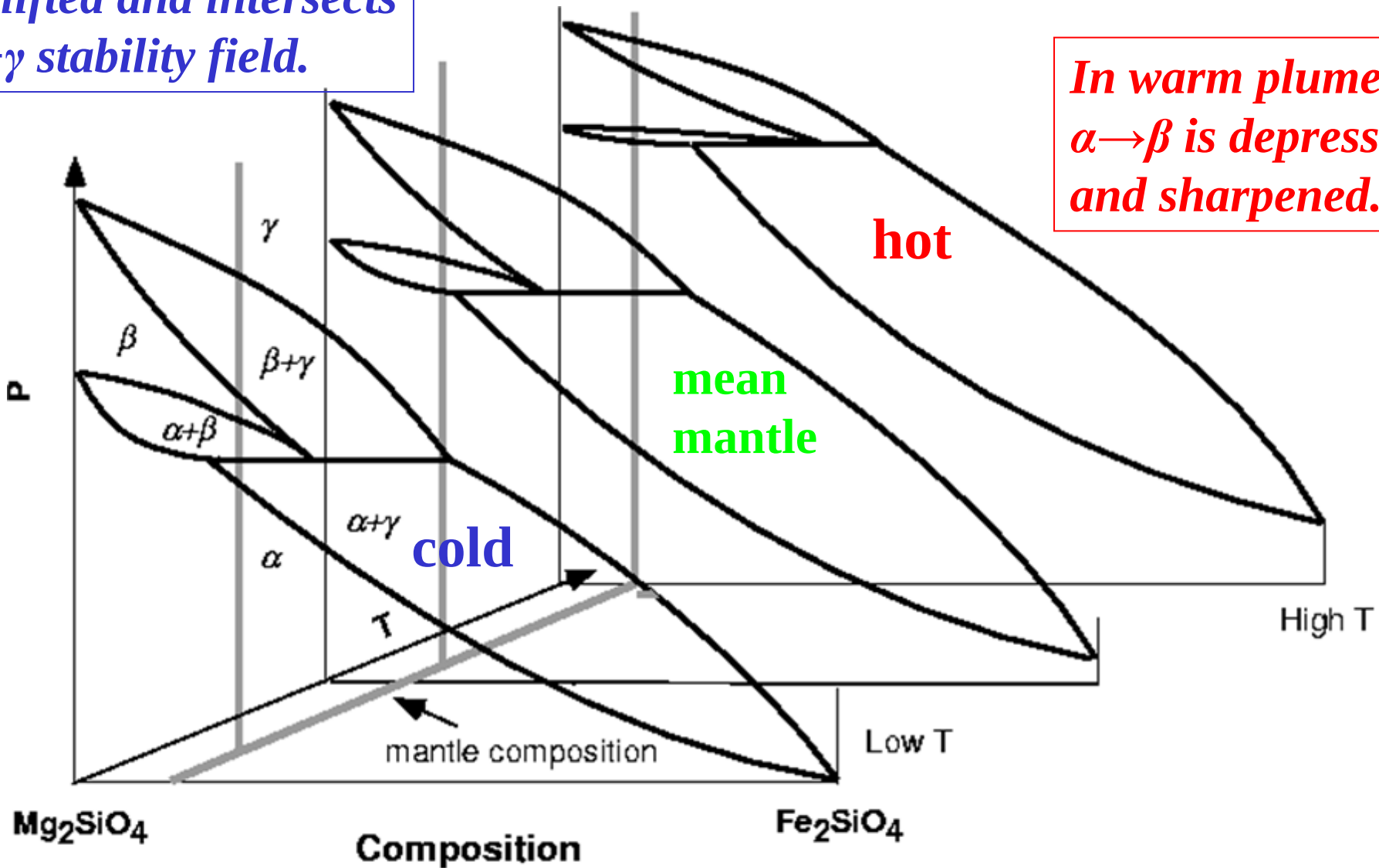


(Figure 16 from Presnall [1995])

Equilibrium Olivine α - β - γ Polymorph Phase Relations

In cold slab, $\alpha \rightarrow \beta$ is uplifted and intersects $\alpha + \gamma$ stability field.

In warm plume, $\alpha \rightarrow \beta$ is depressed and sharpened.



$N=2$

[after Helffrich & Bina, 1994]

Compositions of Coexisting Phases

Consider, for example, a simple binary (*i.e.*, two-component) system A - B in which two phases α and β may coexist. At equilibrium with respect to mass transfer between the phases, the chemical potential of component A must be the same in both phases, and the chemical potential of component B must be the same in both phases, as stipulated in equations (3.8). Hence, we have:

$$\begin{aligned}\mu_A^\alpha(P, T, X_B^\alpha) &= \mu_A^\beta(P, T, X_B^\beta) \\ \mu_B^\alpha(P, T, X_B^\alpha) &= \mu_B^\beta(P, T, X_B^\beta),\end{aligned}\quad \boxed{N=2, R=2: F=2} \quad (4.4)$$

where we have indicated the functional dependence of the chemical potentials upon pressure, temperature, and phase composition. The Gibbs phase rule (4.3) indicates that this system possesses two degrees of freedom. Thus, we may freely vary any two of the unknowns (*e.g.*, P and T), and the remaining variables (*e.g.*, X_B^α and X_B^β) will be fully determined by the constraining equations. Hence, at any fixed pressure and temperature we have two equations (4.4) in two unknowns, X_B^α and X_B^β , so that we may solve for the equilibrium compositions of the two phases. Such

*We know how to find $\mu_i^0(P, T)$, using V_i and $-S_i$,
but how do we find $\mu_i(X_i)$?*

Compositional (Concentration) Dependence of $\mu_i(P,T,X)$

pure component	$(\partial\mu/\partial P)_T = V$	
	$(\partial\mu)_T = V(\partial P)_T$	Ideal gas (EoS): $V = nRT / P$
	$(\partial\mu)_T = (nRT/P)(\partial P)_T$	
	$\Delta\mu^{[P_0 \rightarrow P_i]} = nRT \ln (P_i/P_0)$	Ideal gas (Raoult): $P_i = x_i P_0$
diluted	$\Delta\mu_i^{[1 \rightarrow x_i]} = nRT \ln x_i$	

In general: $\Delta\mu_i^{[1 \rightarrow x_i]} = nRT \ln a_i$ where $a_i = \gamma_i x_i$

$$\mu_i = \mu_i^0 + \Delta\mu_i^{[1 \rightarrow x_i]} = \mu_i^0 + nRT \ln a_i$$

$$\Delta\mu_i = 0 \rightarrow \Delta\mu_i^0 = -RT \ln K_a$$

$$\Delta G^0 = -RT \ln \left[\left(\prod^{\text{products}} a_j^{n_j} \right) / \left(\prod^{\text{reactants}} a_i^{n_i} \right) \right] = -RT \ln K_a$$

activity coefficient

pure state

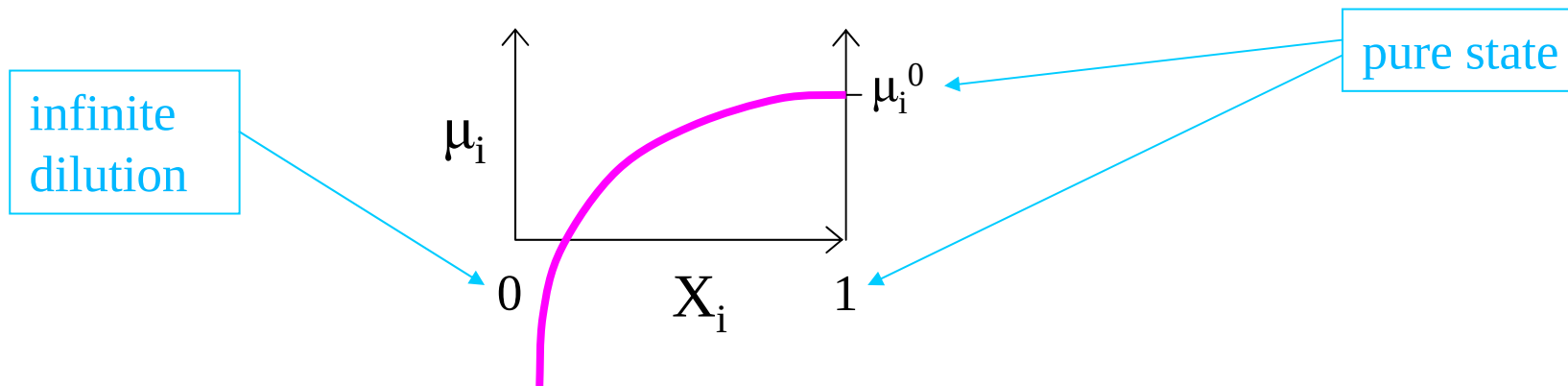
activity

equilibrium constant

Compositional (Concentration) Dependence of $\mu_i(P,T,X)$

$$\mu_i = \mu_i^0 + nRT \ln a_i$$

$$a_i \leq 1 \rightarrow RT \ln a_i \leq 0$$



Dilute solutions have lower chemical potentials (lower free energies) than pure end-members.

Complex solutions have expanded stability fields.

$$(\partial\mu_i^0/\partial T)_P \sim -S_i^0$$

$$(\partial\mu_i/\partial T)_P \sim -S_i^0 + nR \ln a_i$$

entropy of mixing

SOLVING FOR PHASE COEXISTENCE

Two Components ($Fo = \text{Mg}_2\text{SiO}_4$ and $Fa = \text{Fe}_2\text{SiO}_4$):

Two Phases (α and γ): $R = 2 \rightarrow F = 2$ (divariant):

$$\begin{aligned} 0 &= \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T, X_{Fo}^{\alpha}, X_{Fo}^{\gamma}) \\ &= \mu_{Fo}^{\gamma}(P, T, X_{Fo}^{\gamma}) - \mu_{Fo}^{\alpha}(P, T, X_{Fo}^{\alpha}) \\ 0 &= \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T, X_{Fa}^{\alpha}, X_{Fa}^{\gamma}) \\ &= \mu_{Fa}^{\gamma}(P, T, X_{Fa}^{\gamma}) - \mu_{Fa}^{\alpha}(P, T, X_{Fa}^{\alpha}) \end{aligned}$$

For the simplest case, of single-site ideal solution:

$$\begin{aligned} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T, X_{Fo}^{\alpha}, X_{Fo}^{\gamma}) &=^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T) + RT \ln \frac{X_{Fo}^{\gamma}}{X_{Fo}^{\alpha}} \\ ^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T) &\equiv \Delta h_{Fo}^{\alpha \rightarrow \gamma}(P_0, T) - T \Delta s_{Fo}^{\alpha \rightarrow \gamma}(P_0, T) \\ &\quad + \int_{P_0}^P \Delta v_{Fo}^{\alpha \rightarrow \gamma}(\hat{P}, T) d\hat{P} \end{aligned}$$

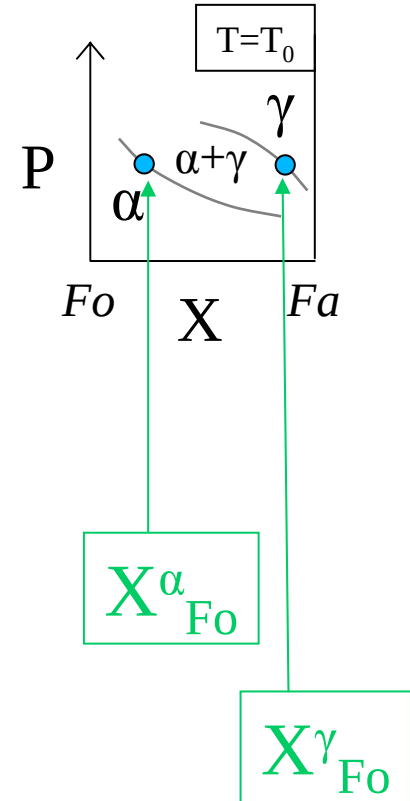
We can find the compositions of the coexisting phases:

$$\begin{aligned} X_{Fo}^{\alpha}(P, T) &= \frac{1 - e^{\frac{-^{\circ} \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T)}{RT}}}{e^{\frac{-^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T)}{RT}} - e^{\frac{-^{\circ} \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T)}{RT}}} \\ X_{Fo}^{\gamma}(P, T) &= e^{\frac{-^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T)}{RT}} \left(\frac{1 - e^{\frac{-^{\circ} \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T)}{RT}}}{e^{\frac{-^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T)}{RT}} - e^{\frac{-^{\circ} \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T)}{RT}}} \right) \end{aligned}$$

[Note that $X_{Fo}^{\alpha}(z)$ and $X_{Fo}^{\gamma}(z)$ are non-linear].



$N=2, R=2: F=2$
 $(N=2, R=2: F'=1)$



Compositions of Coexisting Phases

Consider, for example, a simple binary (*i.e.*, two-component) system A - B in which two phases α and β may coexist. At equilibrium with respect to mass transfer between the phases, the chemical potential of component A must be the same in both phases, and the chemical potential of component B must be the same in both phases, as stipulated in equations (3.8). Hence, we have:

$$\begin{aligned}\mu_A^\alpha(P, T, X_B^\alpha) &= \mu_A^\beta(P, T, X_B^\beta) \\ \mu_B^\alpha(P, T, X_B^\alpha) &= \mu_B^\beta(P, T, X_B^\beta),\end{aligned}\quad \boxed{N=2, R=2: F=2} \quad (4.4)$$

where we have indicated the functional dependence of the chemical potentials upon pressure, temperature, and phase composition. The Gibbs phase rule (4.3) indicates that this system possesses two degrees of freedom. Thus, we may freely vary any two of the unknowns (*e.g.*, P and T), and the remaining variables (*e.g.*, X_B^α and X_B^β) will be fully determined by the constraining equations. Hence, at any fixed pressure and temperature we have two equations (4.4) in two unknowns, X_B^α and X_B^β , so that we may solve for the equilibrium compositions of the two phases.

Relative Proportions of Coexisting Phases

The relative proportions of the α and β phases in the equilibrium phase assemblage can be determined by applying the mass-balance conditions known as the “lever rule” [*cf.* Callen, 1960, pp. 154-156]:

$$X_\alpha^{equil} = \frac{X_B^{bulk} - X_B^\beta}{X_B^\alpha - X_B^\beta}, \quad \boxed{\text{lever rule}} \quad (4.5)$$

where X_B^{bulk} is the mole fraction of component B in the bulk composition of the system, and X_α^{equil} is the mole fraction of phase α in the system at equilibrium.

THE LEVER RULE

Two Components ($Fo = \text{Mg}_2\text{SiO}_4$ and $Fa = \text{Fe}_2\text{SiO}_4$):

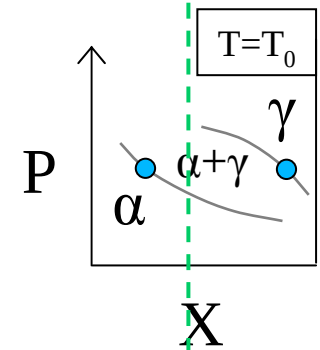
Two Phases (α and γ):

$$\mu_{Fo}^{\alpha}(P, T, X_{Fo}^{\alpha}) = \mu_{Fo}^{\gamma}(P, T, X_{Fo}^{\gamma})$$

$$\mu_{Fa}^{\alpha}(P, T, X_{Fa}^{\alpha}) = \mu_{Fa}^{\gamma}(P, T, X_{Fa}^{\gamma})$$

$R = 2 \rightarrow F = 2$ (divariant)

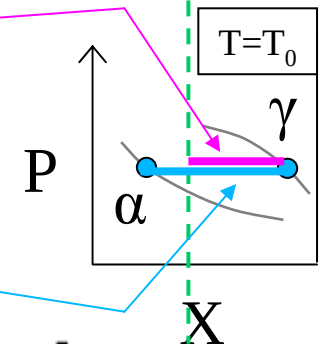
$N=2, R=2: F=2$
 $(N=2, R=2: F'=1)$



We can find the total fraction of Fo in the bulk composition:

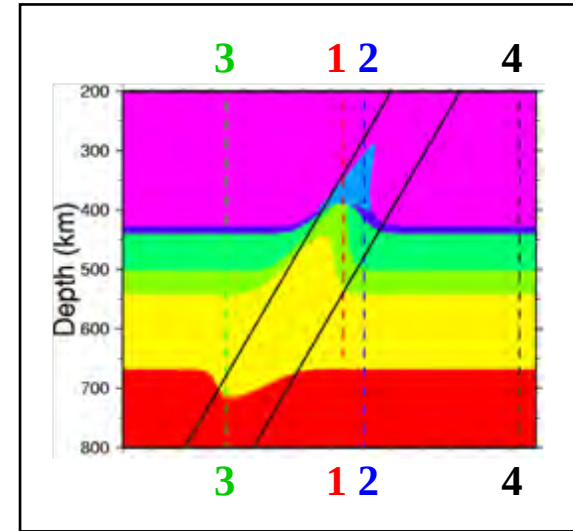
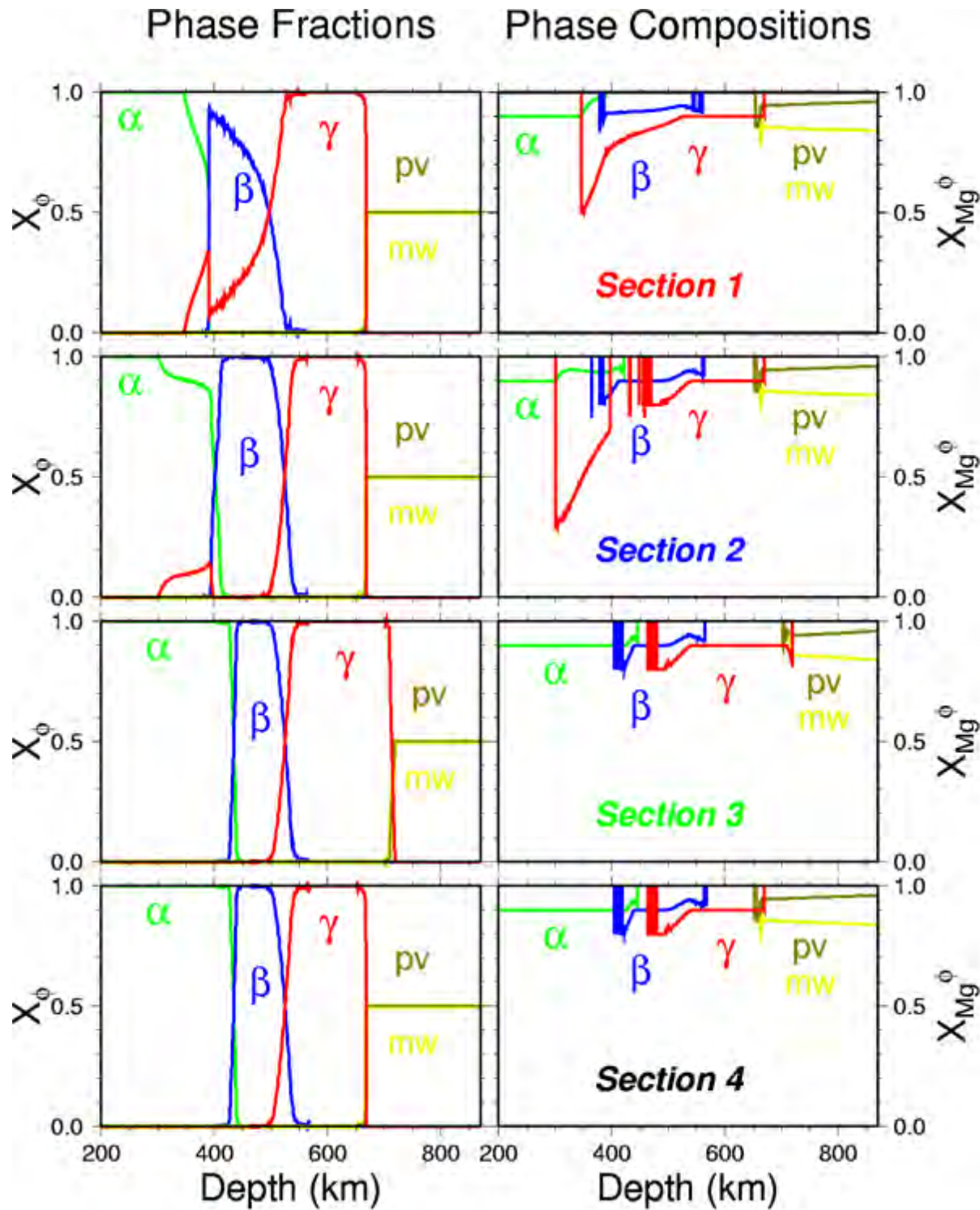
$$X_{Fo}^{BULK} = X_{\alpha} X_{Fo}^{\alpha} + X_{\gamma} X_{Fo}^{\gamma} = X_{\alpha} X_{Fo}^{\alpha} + (1 - X_{\alpha}) X_{Fo}^{\gamma}$$

$$\rightarrow X_{\alpha} = \frac{X_{Fo}^{BULK} - X_{Fo}^{\gamma}}{X_{Fo}^{\alpha} - X_{Fo}^{\gamma}}$$



➔ [Note that both $X_{Fo}^{\alpha}(z)$ and $X_{\alpha}(z)$ are non-linear].

Cross-Sections through a Subduction Zone



(Figures from Bina, 2002)