Interface Transport at Combustion Conditions

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Outline

- Introduction 101
- Energy Partition and Condensation
- Kinetic Theory of Gases
- Correction Parameter α
- Correction Parameter β
- Modeling Results
- Closing Statement

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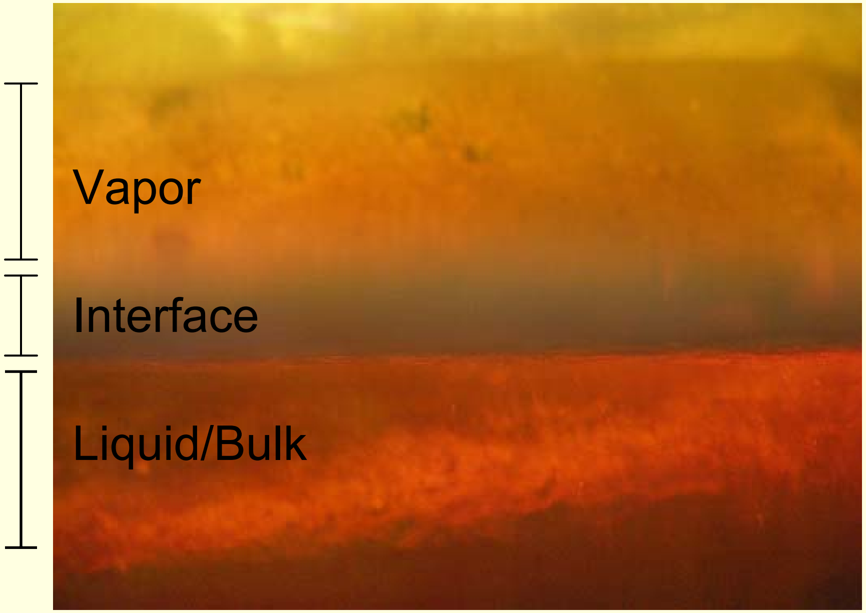
Gas/Liquid Interface

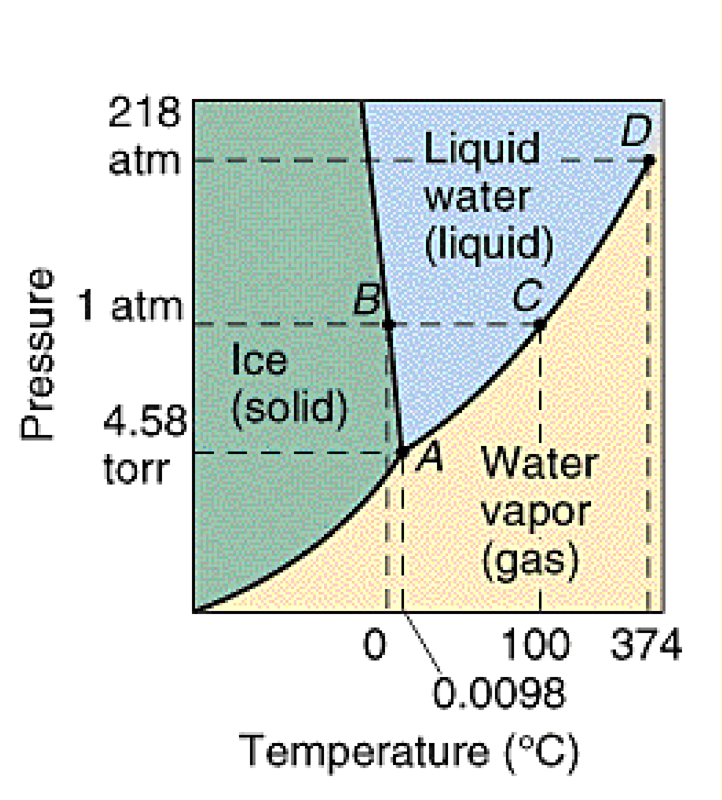
- Distinct separation between a gas and liquid (surface tension)
- Thickness in the nanometer range termed “interface”
- Macroscopic studies consider the surface a two-dimensional

Gas (0^{o}C and 1atm)	**v** (m/s)	**λ** (nm)	**t** (ps)
Carbon Dioxide	380	62.6	185
Methane	600	48.1	80
Hydrogen	1694	110.6	65
Oxygen	425	63.3	149



Gas/Liquid Equilibrium

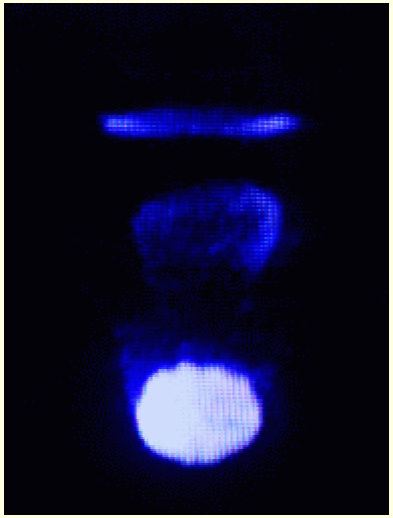
- Interrelate the interfacial compositions using equilibrium assumption
- Adjacent gas and liquid compositions lie on the equilibrium curve
  - Temperatures
  - Partial pressure of vapor assumed equilibrium vapor pressure
  - Heat, momentum and mass fluxes
- Minimum total potential energy



The Interface Equilibrium Enigma

- If temperatures and fluxes of the gas/liquid or gas/solid interface are assumed equal…

There can be no net transfer of heat or mass



Equilibrium Indoctrination

- BSL Evaporation from a freely falling drop
  - “Assume equilibrium at the interface…”
- Wet and dry bulb psychrometer
- Dialysis (membrane separator)
- Wetted-wall column (gas/liquid contact)

Equilibrium Validations

- Interface equilibrium is generally applicable at mild conditions
- Equilibrium simplifies complexity and time required to solve transfer equations
- Equilibrium is not acceptable where conditions of high mass/heat transfer rates exist
- Typified by astringent combustion conditions

$$N_{A0,gas} = N_{A0,liquid} = N_{A0}$$

$$N_{A0,gas} = k(y_{Ax} - y_{A0})$$

$$N_{A0,gas} = \frac{p_{A0}}{\sqrt{2\pi M_A RT}}$$

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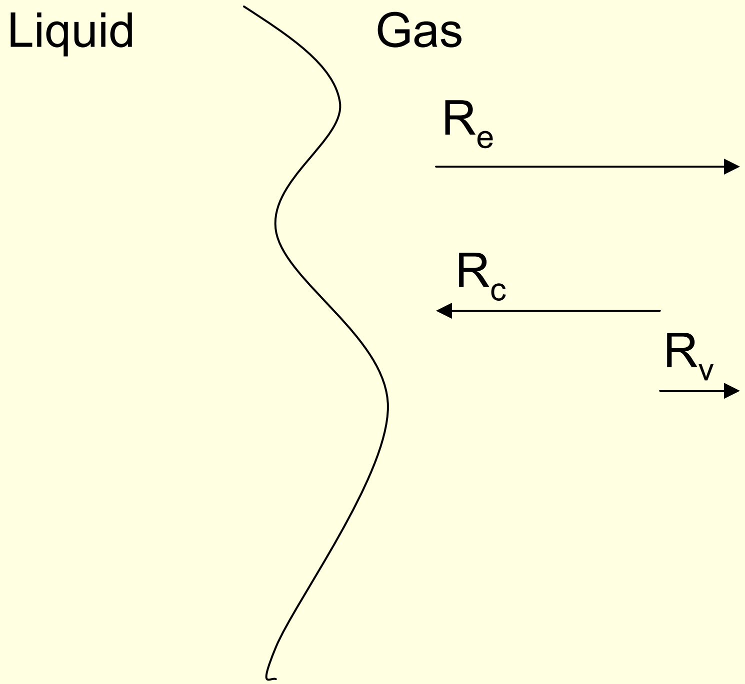
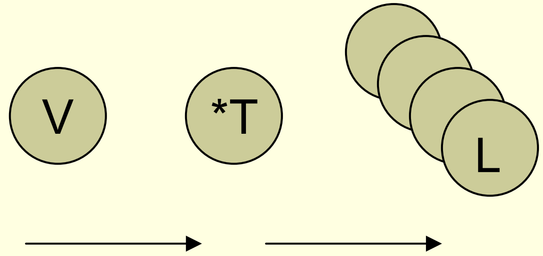
Definition of Vaporization

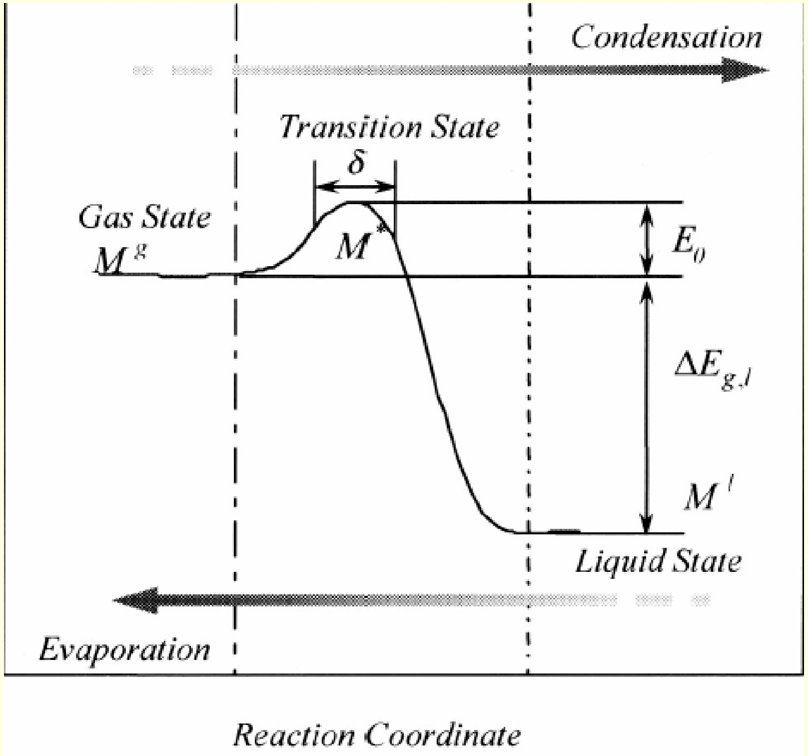
- Condensation – Evaporation =Vaporization



The Process of Condensation

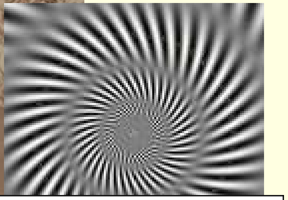
- Transition state (*) occurs at the liquid-vapor interface in the condensation process
- Molecules are assumed to transfer all their energy as they change phases

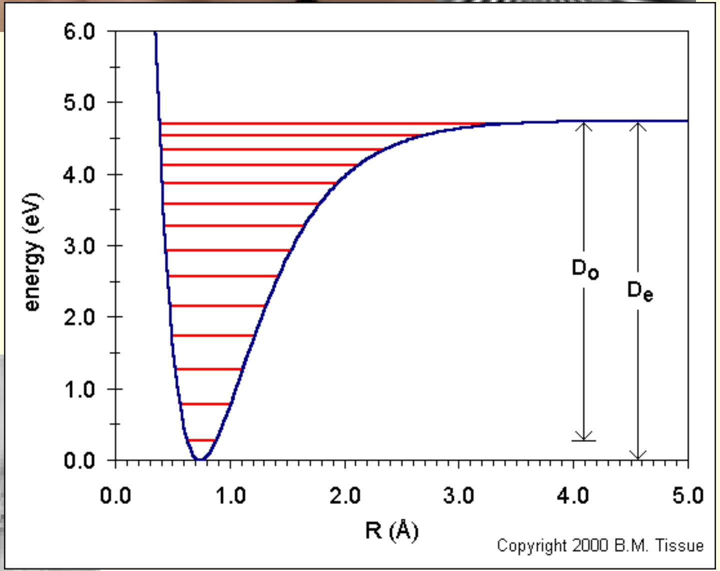




PARTITIONED ENERGY STATES

- Rotational Energy
- Vibrational Energy
  - Violin resonance
- Translational Energy
  - Exchanged by collisions
- Electronic Excitation
  - Neglected





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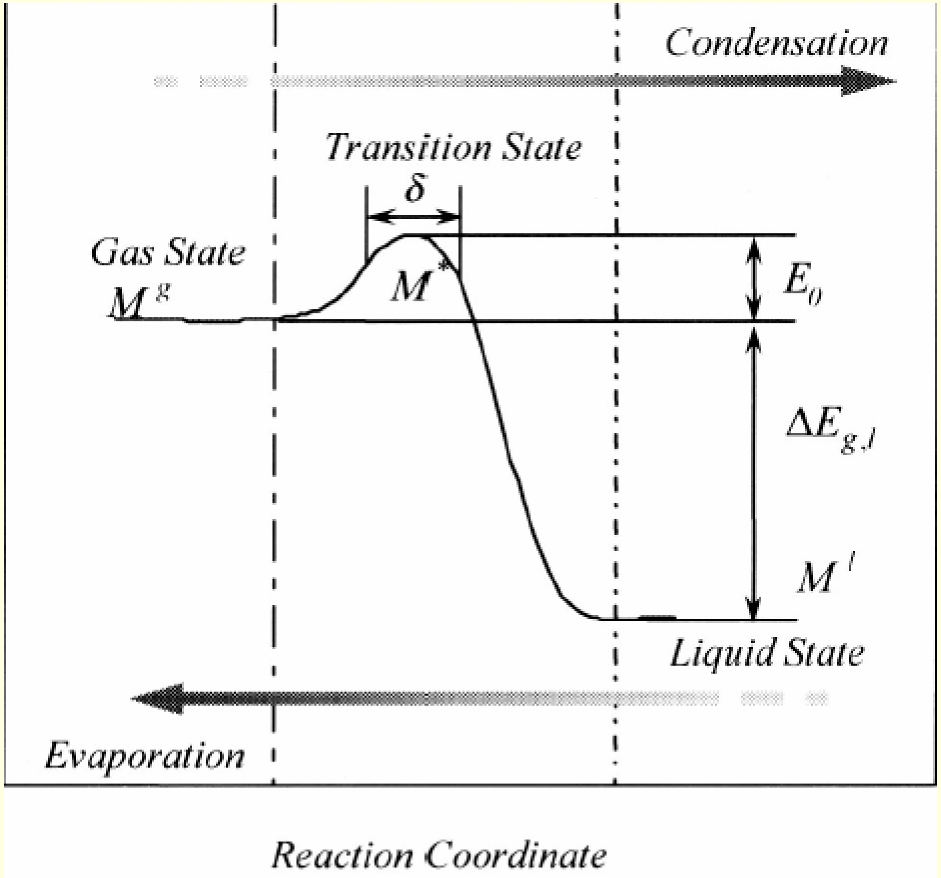
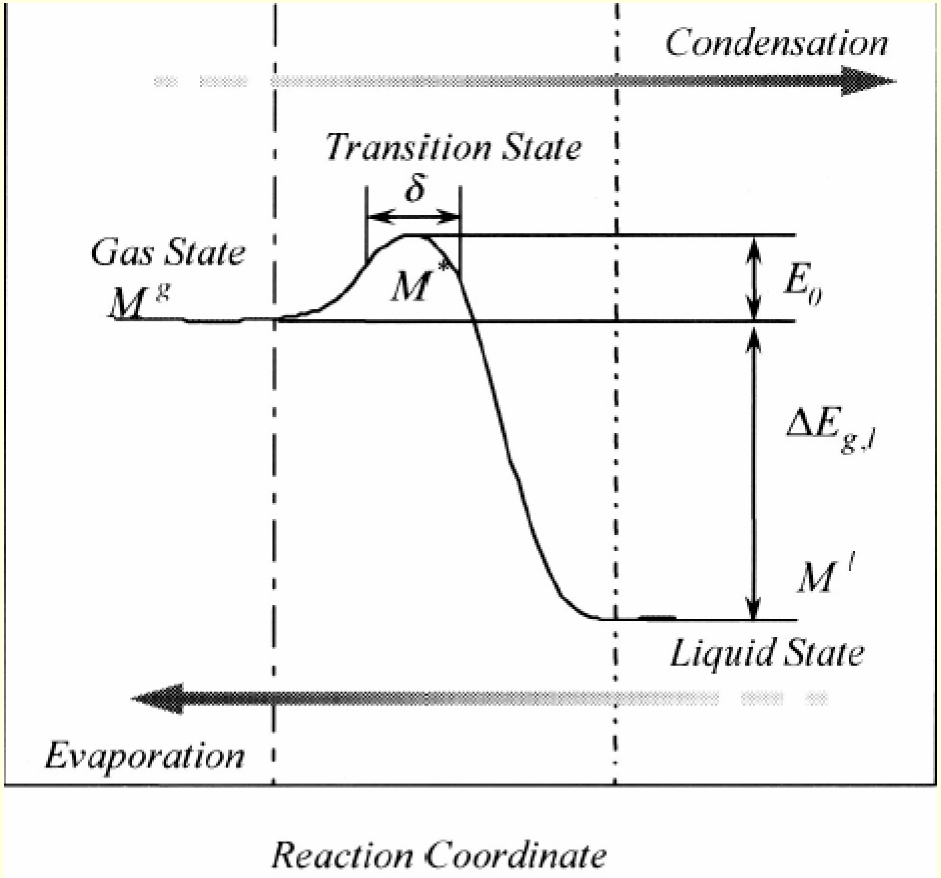
THE PROCESS OF CONDENSATION (TST), cont.

- Rotation inhibited in condensed phase
  - Dipole moment
  - Awkward steric structure
- Condensed rotation likely occurs in concert



THE PROCESS OF CONDENSATION (TST), cont.

- Rotation enhanced in gas phase by same factors which inhibit rotation in the condensed phase
    - Dipole moment
    - Awkward steric structure
- Gas molecules will likely recoil from condensed surface



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Kinetic Theory

- Link between complete dynamic (movement) and statistical (projected/probability) descriptions of gases
- Provides the derivation of or insight into
  - Macroscopic theories
  - Calculation of transport coefficients
  - Phenomena inadequately described by other macroscopic theories

Application of Kinetic Theory

- Average Speed of Gaseous Moving Molecules
  - Slower than a liquid molecule (5-10x)

$$\overline{c_i} = \left(\frac{8RT}{\pi m}\right)^{\frac{1}{2}}$$

- R=universal gas constant
- T=temperature
- M=mass

- Molecular Rate of Collision with a Surface
  - Maxwellian distributed speeds

$$\Gamma_i = \frac{1}{4} n^f \overline{c_i} x_i^f$$

- n=total molar gas concentration
- x=mole fraction of species i

Kinetic Theory Assumptions

- Sole energy contribution is kinetic (motion)
  - no translational, vibrational
- Ceaseless random motion
- Size of molecules is negligible
  - diameters are small compared to average distance between molecules
- Only perfectly elastic collisions
  - no molecular interaction

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Correction Parameter α

- α is the answer to the equilibrium contradiction (gas molecules will likely recoil from the liquid surface)
- α defined as
  - “The mass flux ratio of condensed molecules to all incident molecules upon a liquid surface”
  - “The ratio of the partition functions for the restricted rotation of the molecule in the liquid, and its free rotation in the gas phase”
  - **“The fraction of gas molecules which collide with the condensed phase interface and become part of the condensed phase”**

Correction Parameter α, cont.

- Difference in rotation between liquid and gas phases is reflected in α
- α varies from 0 to 1
  - When α=0, no colliding molecules condense
  - When α=1, all colliding molecules condense
- α decreases with the increase of interface temperature

Correction Parameter α, cont

- Combine α with the kinetic theory's prediction of molecular collision rate
- This will predict the number of colliding molecules which condense into the surface

$$\Gamma_i^c = \alpha_i \frac{1}{4} n^f \overline{c_i} x_i^f \qquad x_i^f = \frac{4\Gamma_i^c}{\alpha_i n^f \overline{c_i}}$$

$$\Gamma_i^v = \Gamma_i^e - \Gamma_i^c = \left(\alpha_i \frac{1}{4} n^f \overline{c_i} x_i^f\right)^e - \left(\alpha_i \frac{1}{4} n^f \overline{c_i} x_i^f\right)^c$$

$$x_i^f = \frac{\alpha_i x_i^s n_s \overline{c_i}^s - 4\Gamma_i^v}{\alpha_i n^f \overline{c_i}^f}$$

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Correction Parameter β

- β is *also* the answer to the equilibrium contradiction!
- β defined as
  - The number of round trips (to and from the interface) that the average molecule would require to transfer an amount of energy γ
  - Inversely proportional to the collision efficiency of a molecule
- β is dependent on the type of molecule, temperature, and composition

$$\gamma \equiv \frac{e^{f} - e^{s}}{e^{f}} = \frac{T^{f} - T^{s}}{T^{f}}$$

Correction Parameter β, cont.

- β ranges from positive unity to infinity
- β=1 when a molecule changes phases
- β is defined for all molecules, whether or not they collide with the interface
- Incorporate β into the rate of molecular collision to represent the rate of transfer of energy (heat)

$$\Gamma^{h} = \sum_{i}^{n} \frac{p_i \overline{c_i}}{2\beta_i} = \sum_{i} n \frac{p_i}{\beta_i} \left(\frac{8RT}{\pi m_i} \right)^{\frac{1}{2}}$$

Correction Parameter β, cont.

- Like done with α, calculate the deviation from equilibrium predicted using the correction parameter β

$$\frac{T^f - T^s}{\left(T^f\right)^{\frac{1}{2}}} = \frac{2q^f \pi^{\frac{1}{2}}}{P(8R)^{\frac{1}{2}} \sum_i \left(\frac{x_i}{m_i \beta_i}\right)^{\frac{1}{2}}}$$

q is the net rate of heat transfer across the interface

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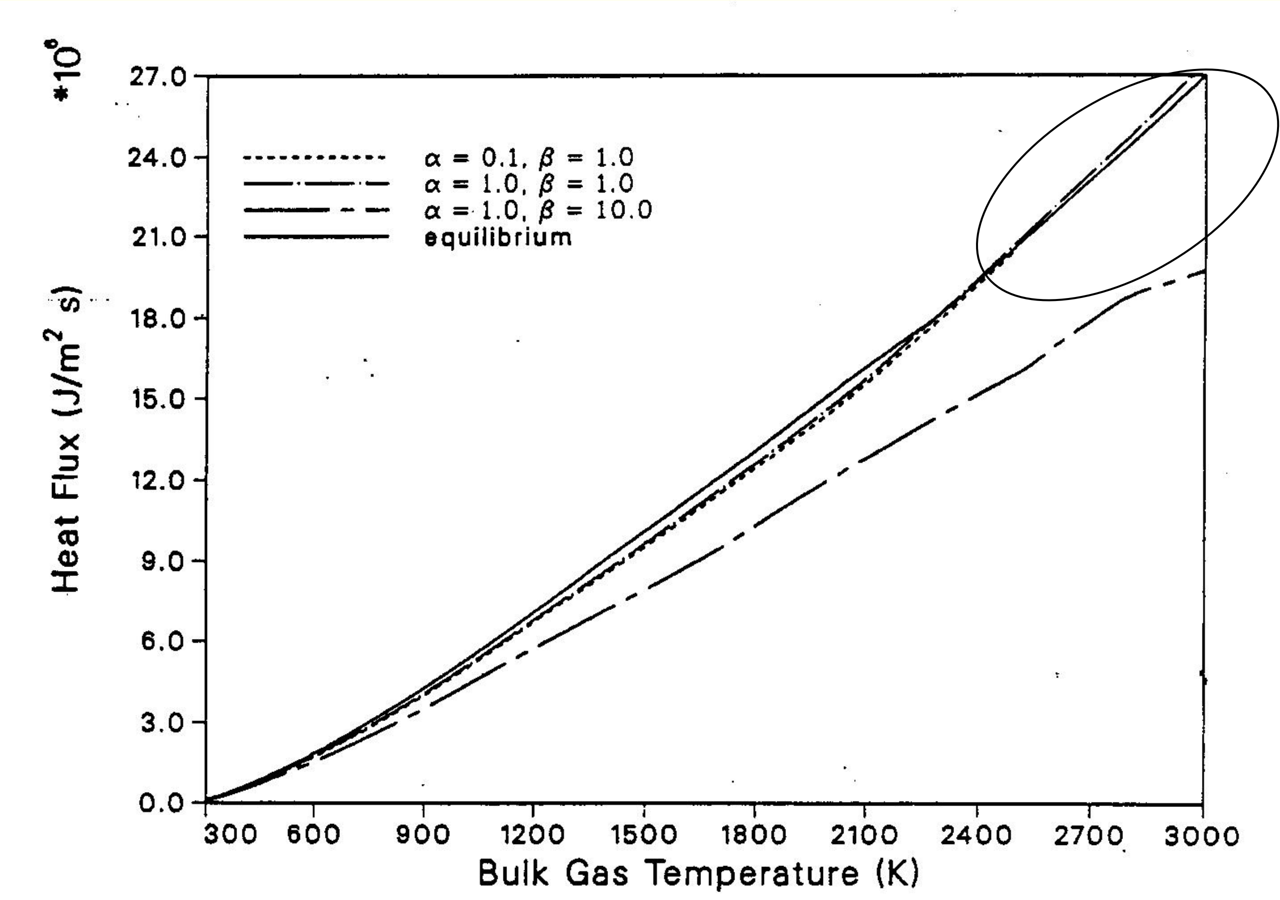
Mathematical Model

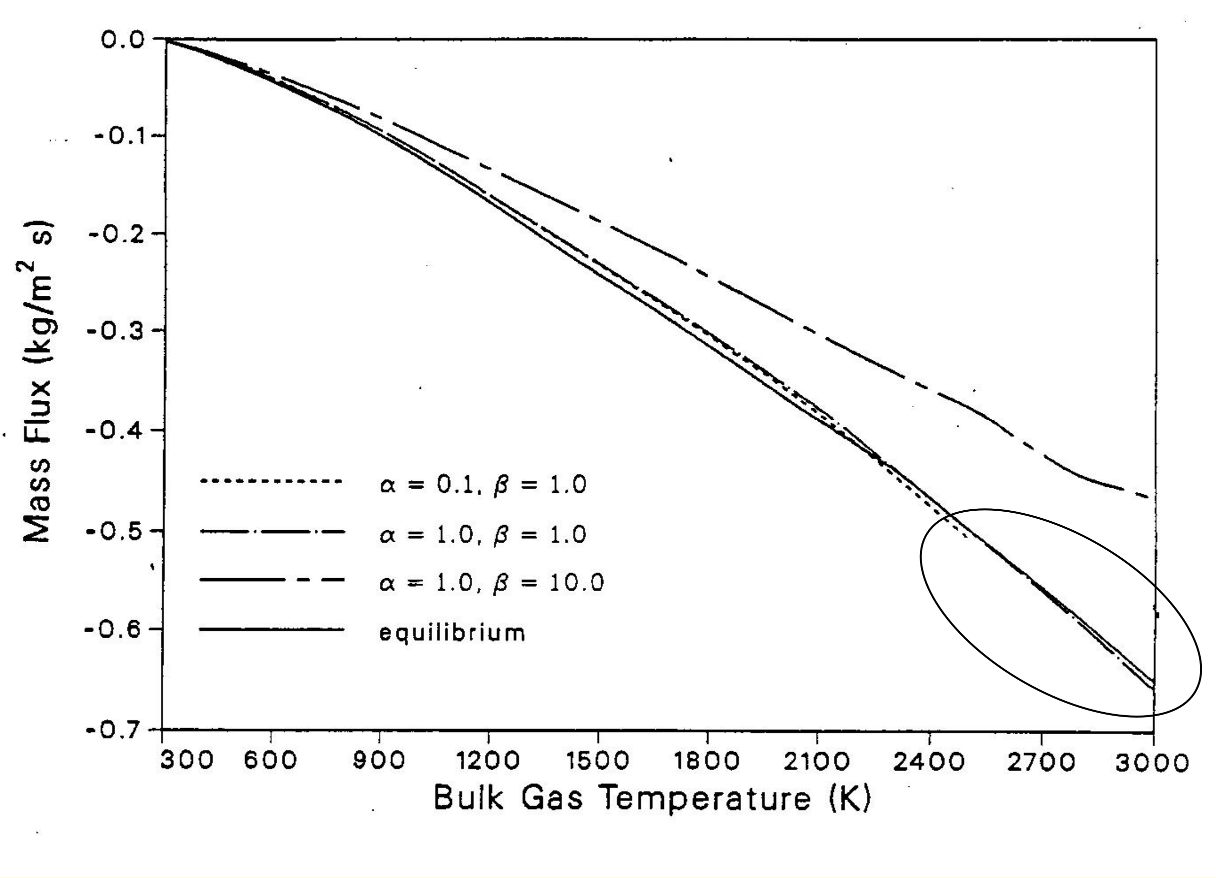
- Experimental and Theoretical Results
  - Nagayama *et. all*
  - Simultaneous solving of mass and heat transfer equations; graphed on MathCAD
- α values as low as 0.01
- β values up to 40.0

$$x_i^f = \frac{\alpha_i x_i^s n^s \overline{c_i}^s - 4\Gamma_i^v}{\alpha_i n^f \overline{c_i}^f}$$

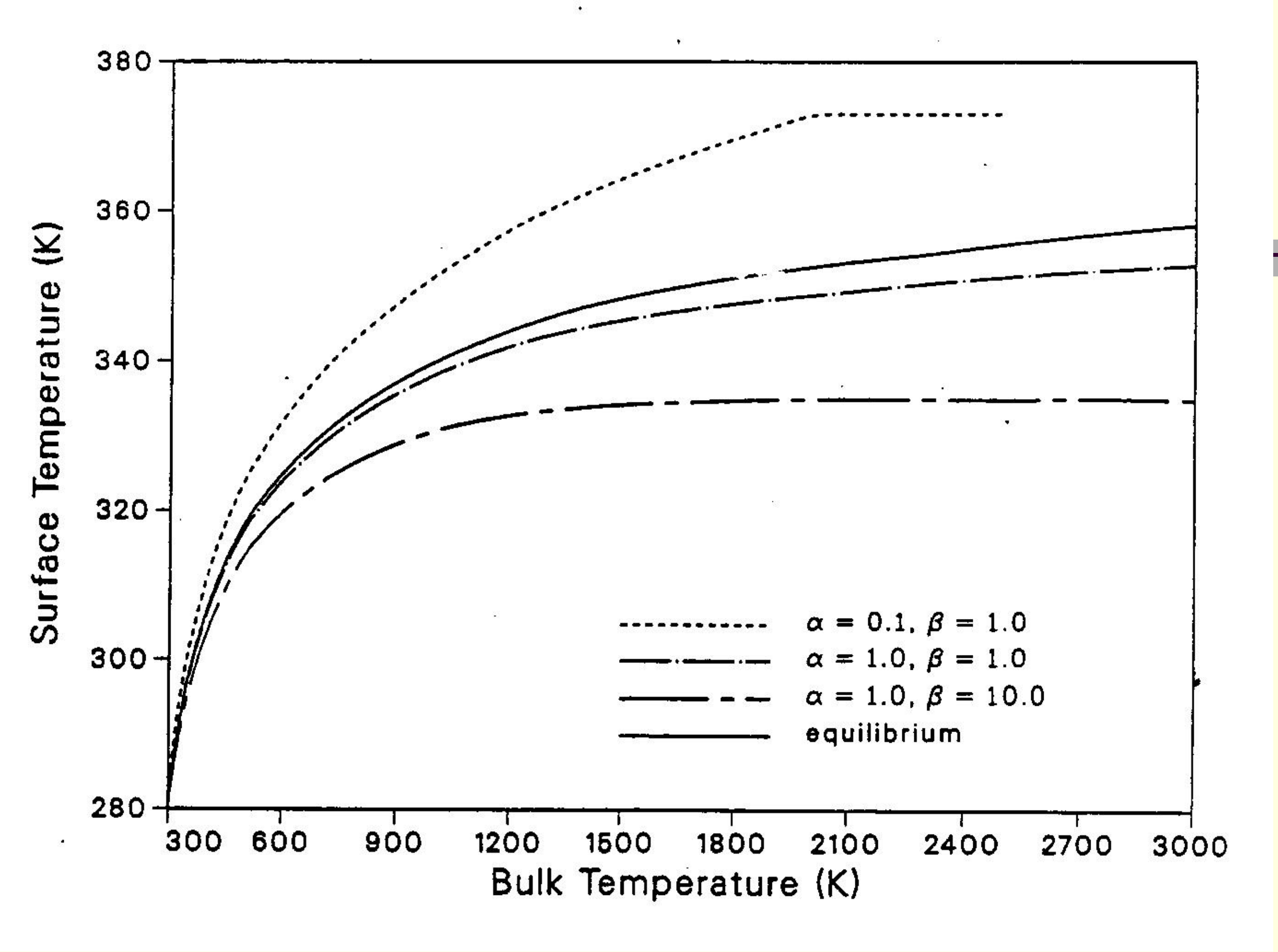
$$\frac{T^f - T^s}{\left(T^f\right)^{\frac{1}{2}}} = \frac{2 q^f \pi^{\frac{1}{2}}}{P(8R)^{\frac{1}{2}} \sum_i \left(\frac{x_i}{m_i \beta_i}\right)^{\frac{1}{2}}}$$



- Rate of heat transfer **to** the droplet (assume heat transfer over mass transfer driven)
- At high temperatures rate exceeds equilibrium assumptions
  - Variation of the transport coefficient (thermal conductivity of gas), gas boundary layer temperatures increase
- Heat transfer decrease of 20% over temperature range
  - This will impact the predicted condensed phase temperatures; transient heat and cooling of particles



- Steady-state mass flux across an interface for several values of α and β (still heat transfer driven)
- Same trends as heat transfer rates (20% decrease) yields equivalent increase in the expected lifetime of a droplet
- Total droplet mass at various points in its lifetime should be measurably larger than predicted assuming equilibrium



- Variations in the steady-state water droplet surface temperature
- Temperatures close to boiling have competing pathways for condensation/vaporization (decrease in α causes an increase in surface temperature)

Representative Values

- Eyring, Schrange, Delany, Mortensen
- Surface Laser Scattering Methods
- Upcoming experimental measurements of β

Species	**α**
CCl_4	1
C_6H6	0.85-0.95
CH_3OH	0.045
H_20	0.036
H_20 (100°C)	0.02
n-C_3H_7OH	0.037
Glycerine	0.052
Ice (H_2O) (-70°C)	0.94

Closing Statement

- α and β help reconcile equilibrium discrepancies
- Approximate trends fit experimental data
- Further experimentation to validate theory