EE-527: MicroFabrication

Physical Vapor Deposition

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R. B. Darling / EE-527
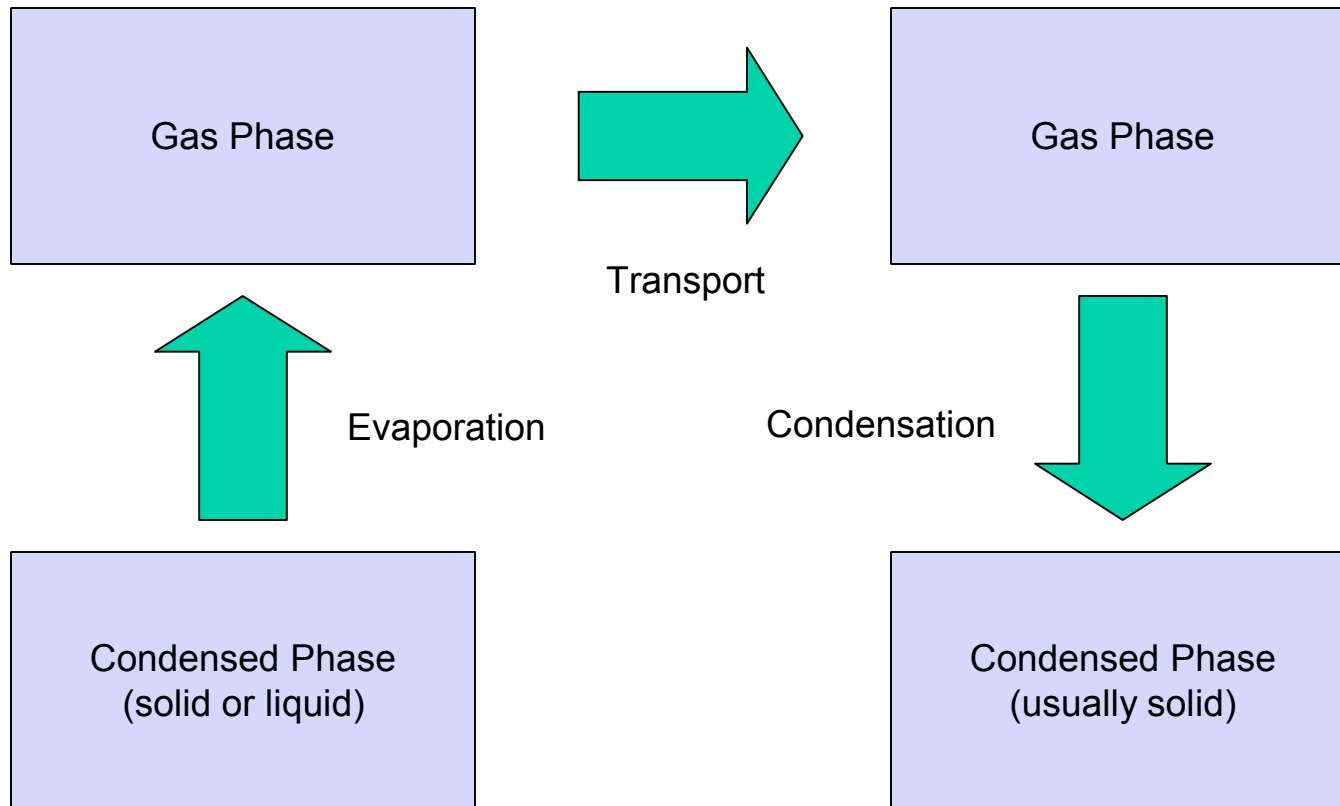
Equilibrium Vapor Pressure

- *P** is the partial pressure of a gas in equilibrium with its condensed phase at a given temperature *T*.
    - No net transfer of material from one state to the other.
- For a given material, *P** is only a function of *T*.
    - But the dependence of *P** on *T* is rather complicated.

Evaporation Rates - 1

- *P** is the equilibrium vapor pressure of the evaporant at T.

- *P* is the ambient hydrostatic pressure acting upon the evaporant in the condensed phase.

- Heinrich Hertz found experimentally that the evaporation rate was proportional to (*P** - *P*).

  - This is consistent with kinetic theory in which the impingement rates are proportional to pressure.

  - Hertz also found that the evaporation rate could not be increased by supplying more heat unless the equilibrium vapor pressure was also increased by this action.

  - Thus, there is a maximum evaporation rate set by *P**, and this is only achieved in a vacuum, where *P* = 0.

Evaporation Rates - 2

- This can be viewed as two opposing fluxes:

evaporant vapor

rate goes as P

rate goes as P^*

condensed evaporant
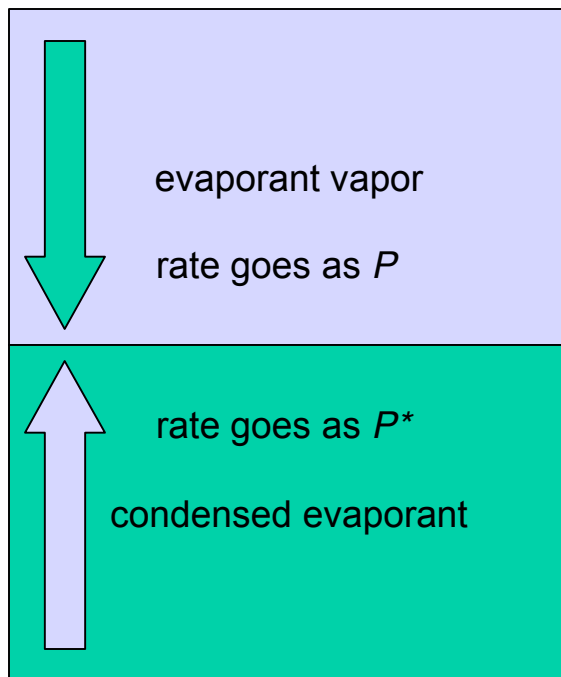
The net evaporation flux is the difference between the impingement rates for the two fluxes:

$$\frac{dN_e}{A_e dt} = \left(2\pi m k_B T\right)^{-1/2}\left(P^* - P\right)$$

Evaporation Rates - 3

- Hertz only measured rates of about 1/10 of the above using Hg vapor.
- Knudsen postulated that the evaporant vapor molecules impinging upon the condensed phase surface may be reflected back.
  - α_v = sticking coefficient for vapor molecules onto the surface.
  - Then a $(1 - \alpha_v)$ fraction of the vapor molecules contribute to the evaporant pressure, but not to the evaporant flux.
  - Therefore, the vapor pressure must be higher by a factor of $1/\alpha_v$ to obtain the same evaporation rate.
- This gives the general Hertz-Knudsen equation:

$$\frac{dN_e}{A_e dt} = \alpha_v \left(2\pi m k_B T\right)^{-1/2}\left(P^* - P\right)$$

Mass Evaporation Rates

- Γ = mass evaporation rate in g/cm^2-sec:

$$\Gamma = m\frac{dN_e}{A_e dt} = \alpha_v \left(\frac{m}{2\pi k_B T}\right)^{1/2} \left(P^* - P\right)$$

- For most elements, $\Gamma \sim 10^{-4}$ g/cm^2-sec at $P^* = 10^{-2}$ torr.
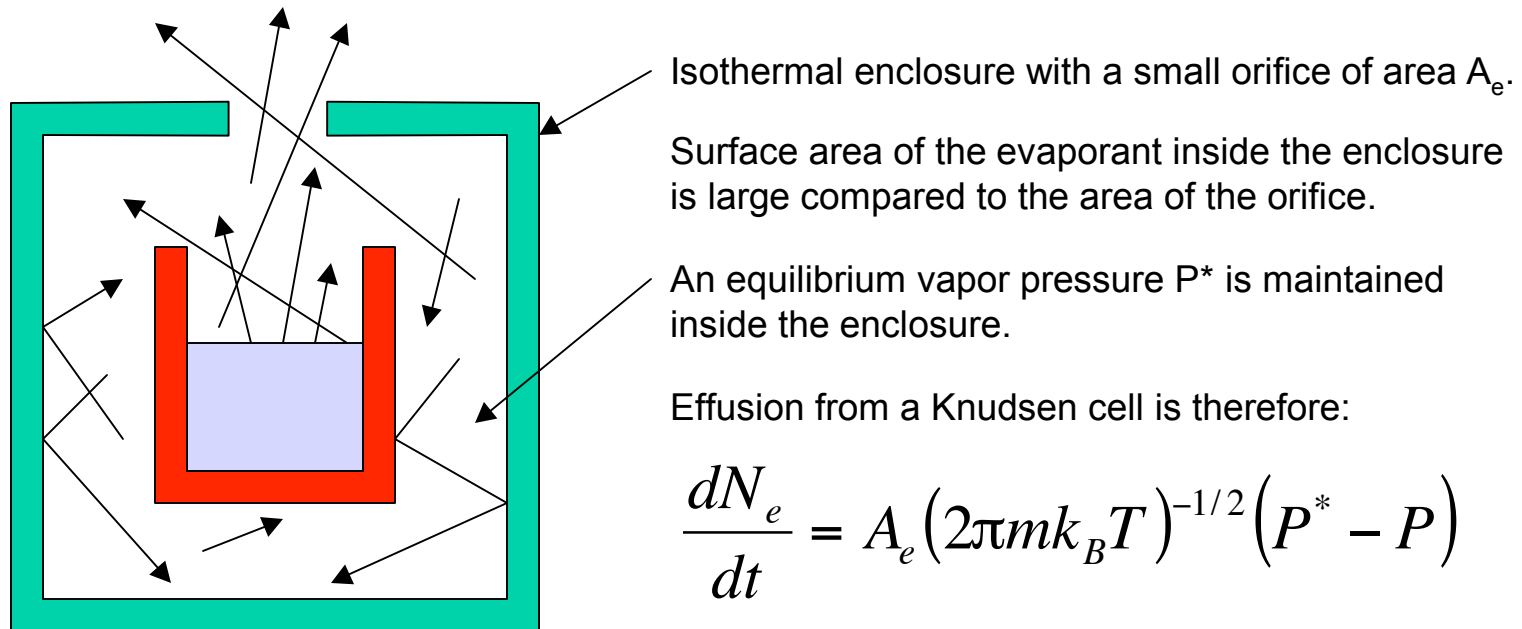- The mass of the evaporated material is

$$M_e = \int_0^t \int_0^{A_e} \Gamma \, dA_e \, dt$$

Free Evaporation Versus Effusion

- Evaporation from a free surface is termed Langmuir evaporation.

- Because α_v is often much less than unity, the general Hertz-Knudsen expression must be used.

- Effusion refers to evaporation through an orifice by which the area of the orifice appears as an evaporation source of the same area.

- Free evaporation is isotropic.

- Effusion is somewhat directional.
 - Ideally, it is a Lambertian angular distribution.

Knudsen Cell

- In 1909 Knudsen invented a technique to force α_v to 1.
- This is called a Knudsen cell, effusion cell, or "K-" cell.
- The orifice acts like an evaporating surface of area A_e at P^*, but it cannot reflect incident vapor molecules, so $\alpha_v = 1$.

Isothermal enclosure with a small orifice of area A_e.

Surface area of the evaporant inside the enclosure is large compared to the area of the orifice.

An equilibrium vapor pressure P* is maintained inside the enclosure.

Effusion from a Knudsen cell is therefore:

$$\frac{dN_e}{dt} = A_e \left(2\pi m k_B T\right)^{-1/2} \left(P^* - P\right)$$

Directional Dependence of a Knudsen Cell - 1

- First find the evaporant flux into a solid angle of $d\omega$ from a source area of dA_e:
  - In a time dt, molecules that are within vdt of the orifice will exit.
  - If molecules are uniformly distributed within the volume V, then the fraction of molecules which are within striking distance in dt of the orifice with an exit angle of φ is $vdt \cos \varphi \, dAe/V$.
  - The fraction of molecules entering the solid angle $d\omega$ is $d\omega/4\pi$.
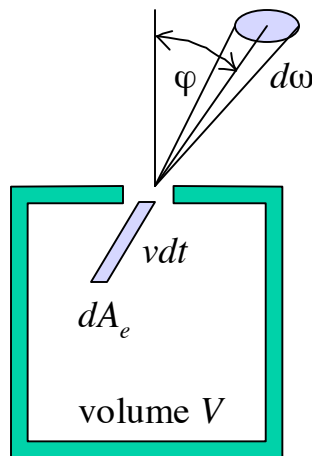
The number of molecules emitted from an area dA_e of the source in a time dt into a solid angle of $d\omega$ about an exit angle of φ with velocities in the range of v to $v + dv$ is:

$$d^4 N_e = N \frac{v \, dt \cos\varphi \, dA_e}{V} \frac{d\omega}{4\pi} \Phi(v^2) \, dv$$

Directional Dependence of a Knudsen Cell - 2

- Integrate over all velocities:
  - A Maxwellian distribution:

$$\Phi(v^2) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T} \right)$$

$$\int_0^\infty v\, \Phi(v^2)\, dv = \sqrt{\frac{4}{\pi}} \left(\frac{2k_B T}{m} \right)^{1/2} = \sqrt{\frac{4}{\pi}}\, v_m = \left(\frac{8k_B T}{\pi\, m} \right)^{1/2}$$

- Obtain:

$$d^3 N_e = \frac{N}{V} \left(\frac{8k_B T}{\pi\, m} \right)^{1/2} \cos\varphi\, dt\, dA_e\, \frac{d\omega}{4\pi}$$

Directional Dependence of a Knudsen Cell - 3

- Since $PV = Nk_BT$, the impingement rate out through the orifice into a solid angle of $d\omega$ about an exit angle of φ is:

$$\frac{d^3 N_e}{dA_e \, dt} = \frac{N}{V}\left(\frac{8k_BT}{\pi \, m}\right)^{1/2}\cos\varphi \, \frac{d\omega}{4\pi} = \left(2\pi m k_B T\right)^{-1/2} P\cos\varphi \, \frac{d\omega}{\pi}$$

- The total impingement rate out through the orifice into <u>all</u> forward solid angles is:

$$\frac{d^2 N_e}{dA_e \, dt} = \left(2\pi m k_B T\right)^{-1/2} P$$

Note that:
$$\int\cos\varphi \, d\omega = \int_0^{2\pi}\int_0^{\pi/2}\cos\varphi \, \sin\varphi \, d\varphi \, d\theta = \pi$$

Directional Dependence of a Knudsen Cell - 4

- The mass evaporation rate through the orifice is

$$\Gamma = m \frac{d^2 N_e}{dA_e dt} = \left(\frac{m}{2\pi \, k_B T} \right)^{1/2} P$$

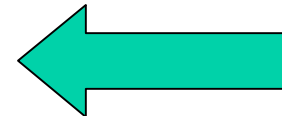- The mass flux into a solid angle of $d\omega$ about an exit angle of φ is thus

$$d^3 M_e = m \, d^3 N_e = \Gamma \cos\varphi \, \frac{d\omega}{\pi} \, dA_e \, dt$$

- The total mass of evaporated material is

$$M_e = \int_0^t \int_0^{A_e} \Gamma \, dA_e \, dt$$

- Cosine law of emission: (Effusion; Lambertian in optics)

$$dM_e = M_e \cos\varphi \, \frac{d\omega}{\pi}$$

- Normalized angular distribution function:

$$f(\varphi,\theta) = \frac{1}{\pi} \cos\varphi \, \sin\varphi \, d\varphi \, d\theta$$
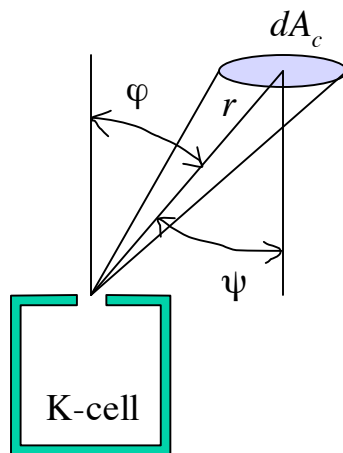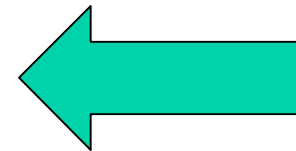
Directional Dependence of Condensation

- The area upon which the evaporant is condensed is
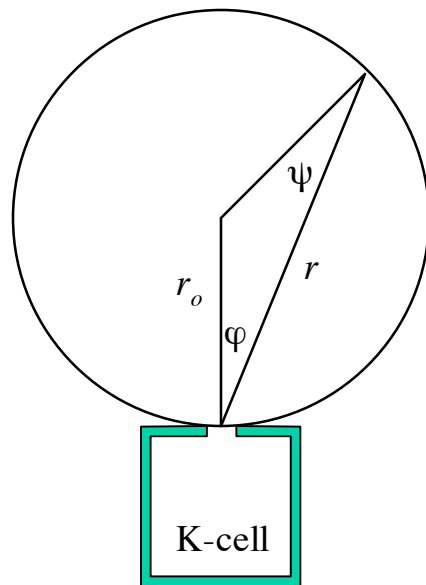
$$dA_c = \frac{r^2 d\omega}{\cos\psi}$$

- The deposited evaporant mass per unit area of condensation surface is thus:

$$\frac{dM_c}{dA_c} = \frac{M_e}{\pi \, r^2} \cos\varphi \, \cos\psi$$

Application of the Cosine Law - 1

- The cosine law was verified by Knudsen by depositing a perfectly uniform coating inside a spherical glass jar:

$$\cos\varphi = \cos\psi = \frac{r}{2r_o}$$

$$\frac{dM_c}{dA_c} = \frac{M_e}{4\pi\, r_o^2} = \text{uniform coating!}$$

This geometry is commercially used for coating the inside surfaces of spherical vessels, e.g. light bulbs, as well as for planetary wafer tooling in vacuum coating equipment.

Application of the Cosine Law - 2

- Uniformity of an evaporated film across a wafer:

$$\frac{dM_c}{dA_c} = \frac{M_e}{\pi\, r^2} \cos\varphi\, \cos\psi$$

substrate wafer

r_w

ψ

r_o

r_e

φ

K-cell
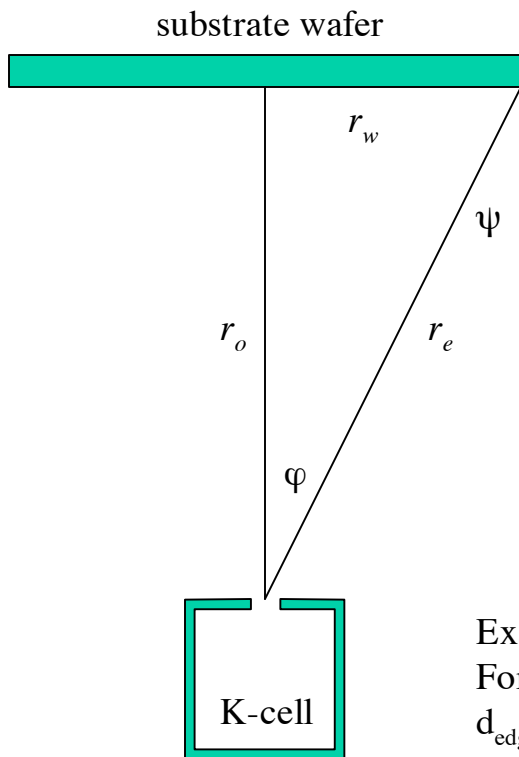
reduction factor for edge thickness:

$$\frac{d_{edge}}{d_{center}} = \frac{r_o^2}{r_o^2 + r_w^2} \cos\varphi\, \cos\psi = \left[\frac{r_o^2}{r_o^2 + r_w^2}\right]^2 = \frac{1}{\left[1+\left(\dfrac{r_w}{r_o}\right)^2\right]^2}$$

Example:
For a 3-inch diameter wafer suspended 18 inches above a Knudsen cell:
$d_{edge}/d_{center} = 0.986$, or a non-uniformity of 1.4 %

Directional Dependence of a Free Point Source

- The evaporated mass from a point source is isotropic:

$$d^3 M_e = \Gamma \, dA_e \, dt \, \frac{d\omega}{4\pi} \qquad\qquad dM_e = M_e \frac{d\omega}{4\pi}$$

- For a condensation surface of $dA_c = r^2 d\omega/\cos\psi$, obtain:

$$\frac{dM_c}{dA_c} = \frac{M_e}{4\pi \, r^2} \cos\psi$$

- To put a uniform coating inside a spherical surface, a point source must be located at the center of the sphere.

Thermodynamic Potentials - 1

- $U = U(S,V,N_1,N_2,\ldots,N_r)$ is the internal energy of a system of particles.

  - S = entropy

  - V = volume

  - N_1, N_2, $\ldots$,N_r are the number of particles in each of r components.

- For a monoatomic gas,

  - Equation of state: $PV = NRT$

  - Internal energy is $U = 3/2\ NRT$

- U is a measure of the potential for work by the system.

Thermodynamic Potentials - 2

$$\left. \frac{\partial U}{\partial S} \right|_{V, N_1 \ldots N_r} = T = \text{temperature}$$

$$-\left. \frac{\partial U}{\partial V} \right|_{S, N_1 \ldots N_r} = P = \text{pressure}$$

$$\left. \frac{\partial U}{\partial N_j} \right|_{S, V, N_i \neq N_j} = \mu_j = \text{electrochemical potential}$$

$$dU = TdS - PdV + \mu_1 dN_1 + \cdots + \mu_2 dN_2$$

Thermodynamic Potentials - 3

- ## Helmholtz potential:
  - $F = F(T,V,N_1,N_2,\ldots,N_r) = U - TS$
  - potential for work by system at constant temperature

- ## Enthalpy:
  - $H = H(S,P,N_1,N_2,\ldots,N_r) = U + PV$
  - potential for work by system at constant pressure
  - examples: heat engines, turbines, diesel motors

- ## Gibbs free energy:
  - $G = G(T,P,N_1,N_2,\ldots,N_r) = U - TS + PV$
  - potential for work by system at constant temperature and pressure
  - examples: chemical reactions, electrochemistry

Maxwell Relations

$$\left.\frac{\partial V}{\partial S}\right|_P = \left.\frac{\partial T}{\partial P}\right|_S$$

$$\left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P$$

$$\left.\frac{\partial P}{\partial T}\right|_V = \left.\frac{\partial S}{\partial V}\right|_T$$

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

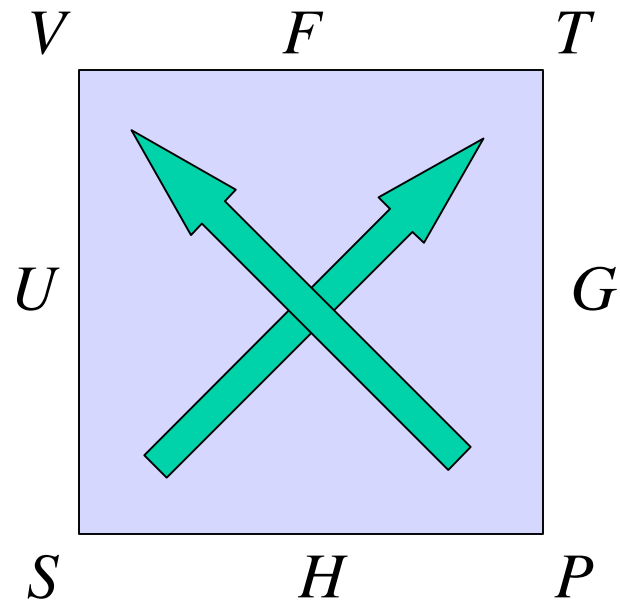$$dU = TdS - PdV + \sum_k \mu_k dN_k$$

$$dF = -SdT - PdV + \sum_k \mu_k dN_k$$

$$dG = -SdT + VdP + \sum_k \mu_k dN_k$$

$$dH = TdS + VdP + \sum_k \mu_k dN_k$$
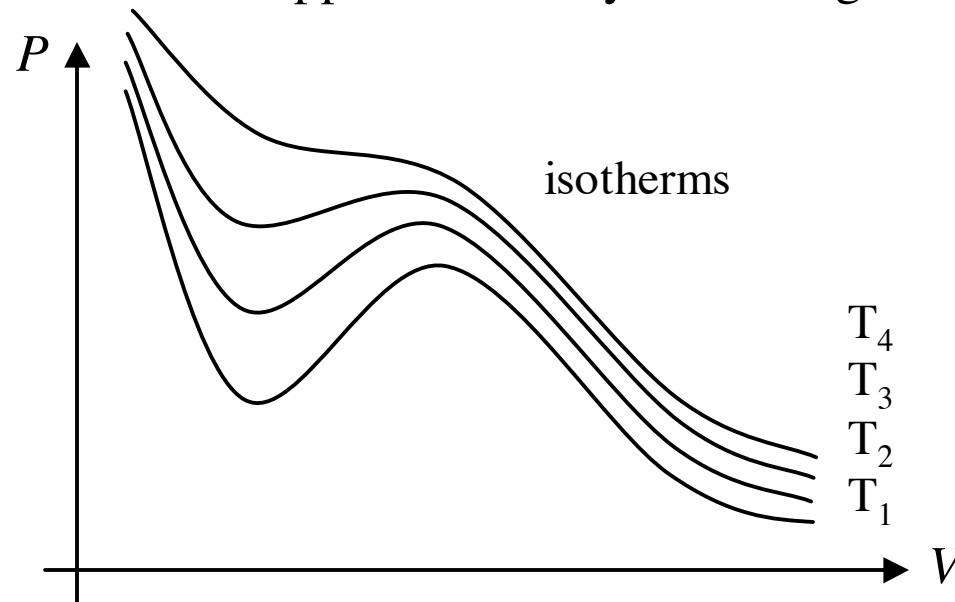
Mnemonic Diagram

- Originally due to Max Born:
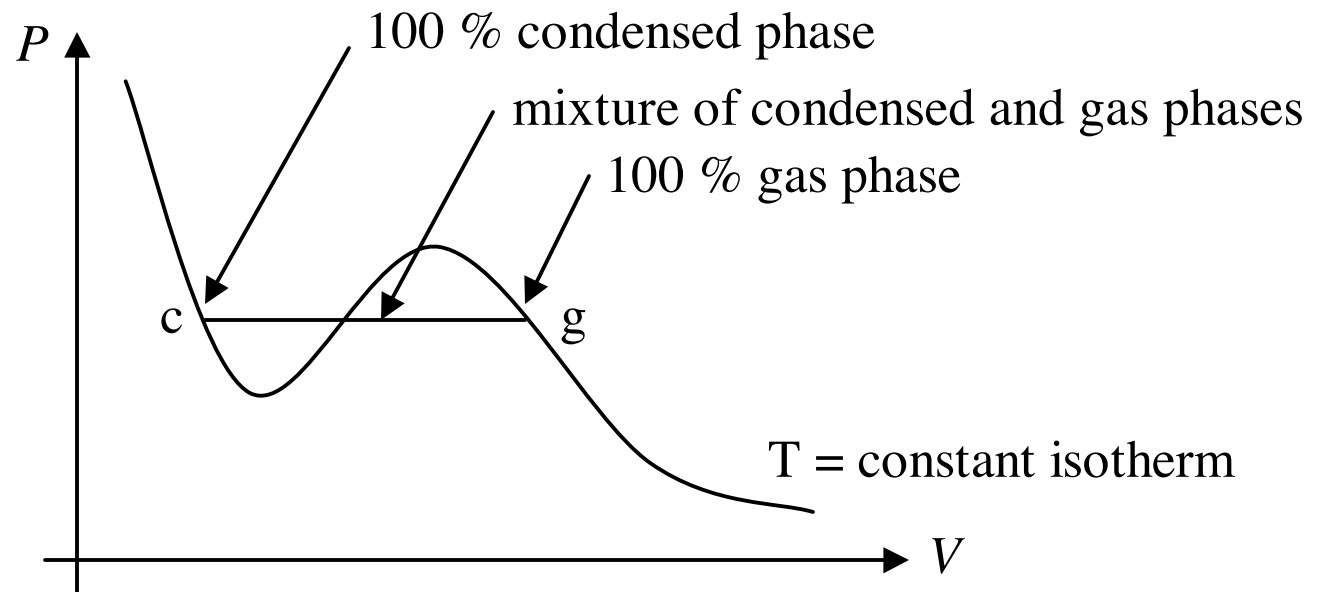
van der Waals Equation of State

$$P = \frac{NRT}{V - bN} - \frac{aN^2}{V^2}$$

- {a,b} are van der Waals parameters.
- For large volumes and small particle numbers, van der Waals equation of state is approximated by the ideal gas law: $P = NRT/V$.
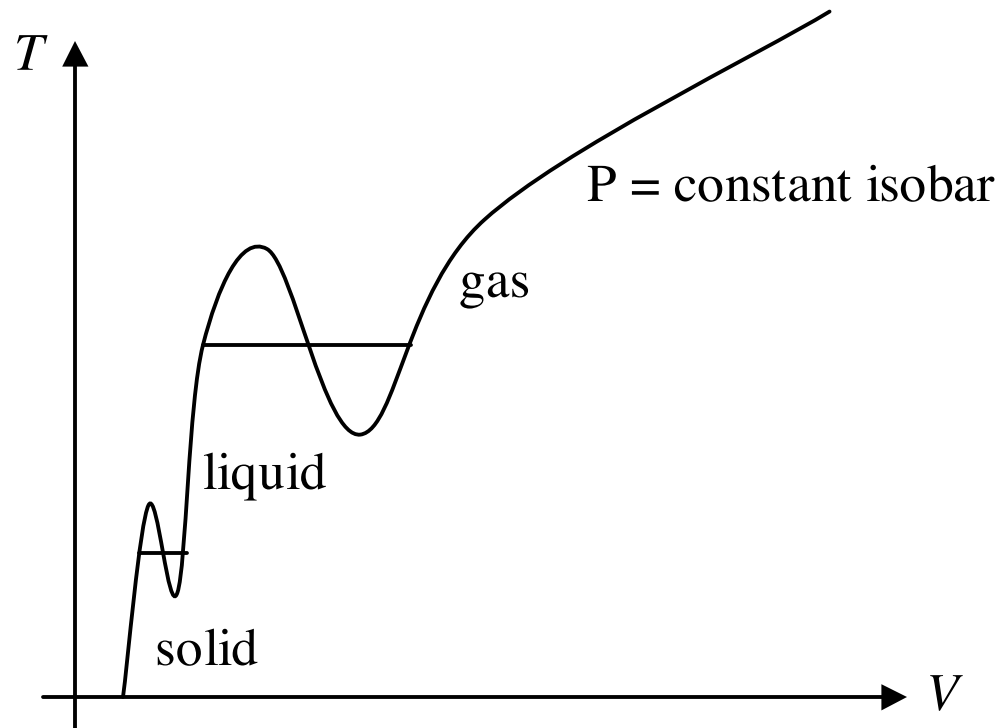
Phase Transitions - 1

- A system will only remain homogeneous if certain thermodynamic stability criteria are met. If not, it will separate into two or more portions.

100 % condensed phase

mixture of condensed and gas phases

100 % gas phase

P

c   g

T = constant isotherm

V

Phase Transitions - 2

- Similarly:

Phase Transitions - 3

- Internal energy = $U = U(S,V,N)$
  - $dU = TdS - PdV + \mu dN$, in general.
  - No material is created or destroyed during a phase transition: $dN = 0$.
- $\Delta U = U_g - U_c = T(S_g - S_c) - P(V_g - V_c)$
  - $\Delta U = L_{gc} - P(V_g - V_c)$,
  - where $L_{gc} = T(S_g - S_c)$ is the latent heat of the phase transition.
- For water:
  - At 0°C the latent heat of fusion is 80 cal/g = 1440 cal/mole
  - At 100°C the latent heat of vaporization is 540 cal/g = 9720 cal/mole

Equilibrium Vapor Pressure - 1

- Pressure of a gas in equilibrium with its condensed phase.
- Evaporation of the condensed phase converts thermal energy into mechanical energy (expansion of the vapor).
- Process is less than 100 % efficient, because some thermal energy must be used to increase the entropy of the system.
  - (Second Law of Thermodynamics)

Equilibrium Vapor Pressure - 2
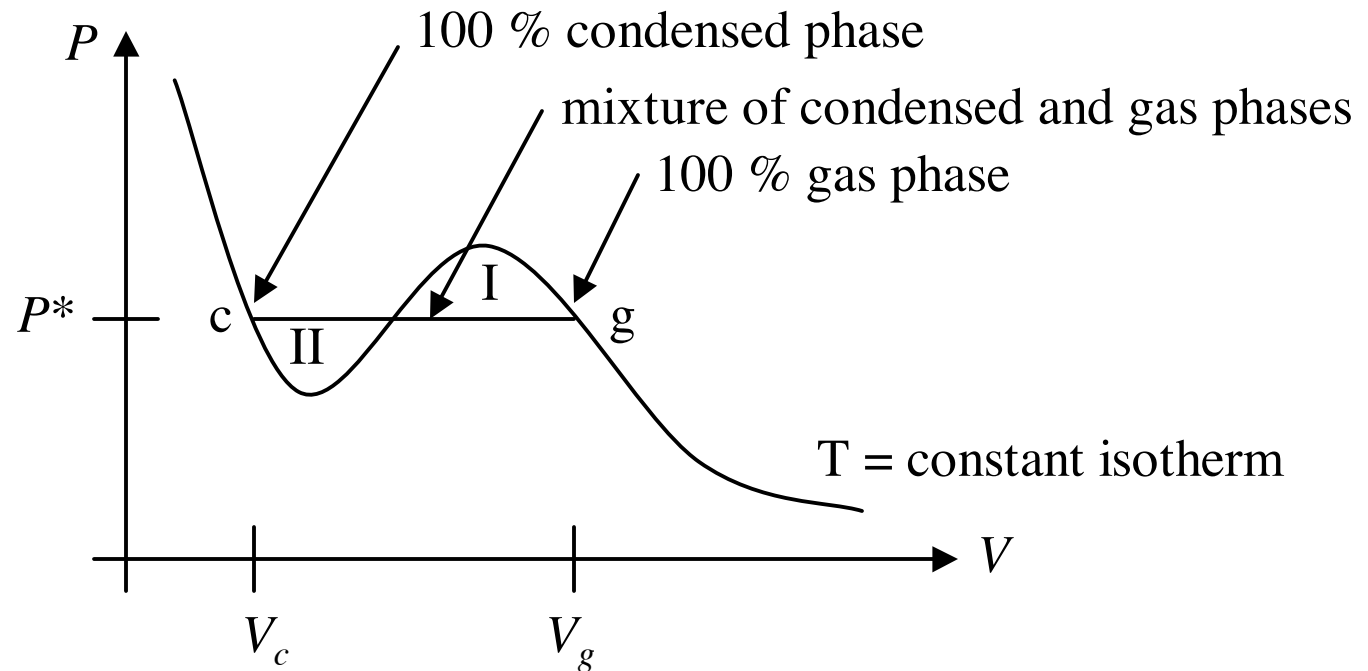
$P*$ is the pressure which makes areas I and II equal.

Equilibrium Vapor Pressure - 3

- Need to integrate along the isotherm to find $\Delta S = S_g - S_c$.
- In general,

$$dS = \left.\frac{\partial S}{\partial V}\right|_T dV + \left.\frac{\partial S}{\partial T}\right|_V dT$$

- Temperature is constant during the phase change, so:

$$dS = \left.\frac{\partial S}{\partial V}\right|_T dV = \left.\frac{\partial P}{\partial T}\right|_V dV$$

  - (Using the Maxwell relation)

- $(\partial P/\partial T)_V$ is independent of volume during the phase transition, so

$$\frac{\partial P}{\partial T} \rightarrow \frac{dP^*}{dT}$$

- P^* is a function of only T.

Equilibrium Vapor Pressure - 4

- Integrating along the isotherm then produces

$$\frac{dP^*}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_g - S_c}{V_g - V_c}$$

- The latent heat of the phase transition is $L_{gc} = T(S_g - S_c)$.

- Substituting gives the Clapeyron Equation:

$$\frac{dP^*}{dT} = \frac{L_{gc}}{T(V_g - V_c)}$$

- For low vapor pressures, V_g - $V_c \approx V_g \approx NRT/P$, which gives the Clausius-Clapeyron Equation:

$$\frac{dP^*}{P^*} = \frac{L_{gc}dT}{NRT^2}$$

Equilibrium Vapor Pressure - 5

- If L_{gc} is constant with temperature, integrating the Clausius-Clapeyron equation produces an Arrhenius relationship for the equilibrium vapor pressure:

$$\ln P^* = -\frac{L_{gc}}{NRT} + C_1$$

$$P^* = C_2 \exp\left(-\frac{L_{gc}}{NRT}\right)$$

- L_{gc}/N is tabulated for many substances, but it does have a temperature dependence which can alter the above integration.

Equilibrium Vapor Pressure - 6

- The heat capacity of a material at constant pressure is:

$$c_p = \frac{\partial H}{\partial T} = a + bT + cT^2 + dT^{-2}$$

  - The {a,b,c,d} parameters are given in tables of thermochemical data, e.g. the CRC Handbook of Chemistry and Physics.

- Integrating over temperature gives the temperature dependence of the latent heat of the phase transition:

$$L_{gc} = L_{gco} + \int_{T_0}^{T} (c_{pg} - c_{pc}) \, dT = L_{gco} + \Delta aT + \tfrac{1}{2}\Delta bT^2 + \tfrac{1}{3}\Delta cT^3 - \frac{\Delta d}{T}$$

Equilibrium Vapor Pressure - 7

- Integrating $L_{gc}(T)$ in the Clausius-Clapeyron equation gives:

$$\ln P^* = -\frac{L_{gco}}{NRT} + \frac{\Delta a}{NR}\ln T + \frac{\Delta bT}{2NR} + \frac{\Delta cT^2}{6NR} + \frac{\Delta d}{2NRT^2} + C_3$$

  – Both L_{gco} and C_3 are unknown integration constants.

- Standard thermochemical data is specified at a "standard" state of 1 atmosphere of pressure and a temperature of 25°C or 298.15 K, the triple point of water.

  – Need to rephrase the Clausius-Clapeyron equation to be able to use this data.

  – The standard state of temperature and pressure (STP) is usually denoted by a "0" subscript or superscript.

Equilibrium Vapor Pressure - 8

- Standard state chemical potentials for the gas and condensed phases are μ_{go} and μ_{co}.
- Equilibrium at a given temperature occurs by letting the chemical potentials change until they equal each other at the equilibrium vapor pressure of $P*$:

$$\mu_{go}(T) + \int_{1\,atm}^{P*} \left(\frac{\partial \mu_g}{\partial P} \right)_T dP = \mu_{co}(T) + \int_{1\,atm}^{P*} \left(\frac{\partial \mu_c}{\partial P} \right)_T dP$$

- The molar volume is given as shown, and for an ideal gas,

$$\left(\frac{\partial \mu_g}{\partial P} \right)_T = \frac{V_g}{N} = \frac{RT}{P}$$

- Since V_c is small, the integral for the condensed phase can be ignored.

Equilibrium Vapor Pressure - 9

- Integrating gives the standard free energy of evaporation:

$$\Delta G_{eo}(T) = \mu_{go}(T) - \mu_{co}(T) = -RT \ln P^{*}$$

  - P^{*} is expressed in atmospheres.
  - This now gives an expression for P^{*} which eliminates the unknown integration constants, but ΔG_{eo} is only listed for 298 K.

- Use the facts that:

$$G = H - TS, \qquad \left(\frac{\partial \Delta G_{eo}}{\partial T}\right)_{P} = -\Delta S_{eo}(T), \qquad \left(\frac{\partial \Delta S_{eo}}{\partial T}\right)_{P} = \frac{c_{p}}{T}.$$

- Integrate twice to obtain:

$$\Delta G_{eo}(T) = \Delta H_{eo}(298K) - T\Delta S_{eo}(298K) - \int_{298K}^{T}\int_{298K}^{T} \frac{\Delta c_{p}}{T} \, dT dT$$
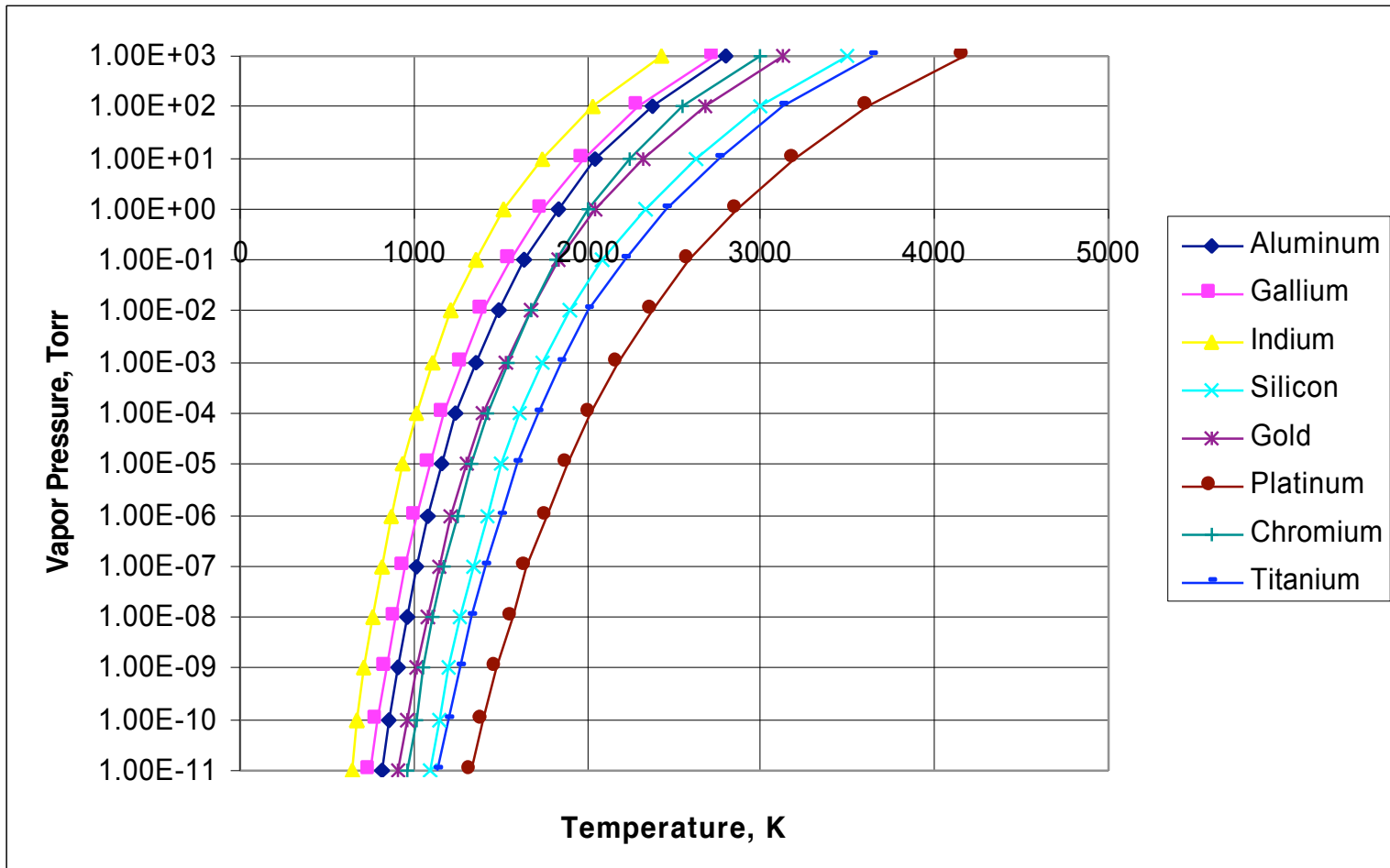
Equilibrium Vapor Pressure - 10

- A working formulation of the equilibrium vapor pressure from standard thermochemical data is therefore:

$$\ln P^* = -\frac{\Delta H_{eo}(298K)}{RT} + \frac{\Delta S_{eo}(298K)}{R} + \frac{1}{RT}\int_{298K}^{T}\int_{298K}^{T}\frac{\Delta c_p}{T}dTdT$$

  - P^* is in units of atmospheres.
  - $\Delta H_{eo}(298K)$, $\Delta S_{eo}(298K)$, and $c_p(T)$ may be found in standard tables of thermochemical data.
  - Note: 1 kcal = 1 Cal = 1000 cal = 4186.8 J = 3.97 BTU
  - See Section D of the CRC Handbook of Chemistry and Physics.
  - Example: Aluminum:
    - $\Delta H_{eo}(298K)$ = 70 kcal/mole, $\Delta S_{eo}(298K)$ = 30 kcal/mole-K, at the boiling point of P = 1 atm and T = 2327°C = 2600 K.
    - $\Delta H_{mo}(298K)$ = 2.57 kcal/mole, at the melting point of P = 1 atm and T = 658.5°C = 931.7 K.

Equilibrium Vapor Pressure - 11

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Equilibrium Vapor Pressure - 12

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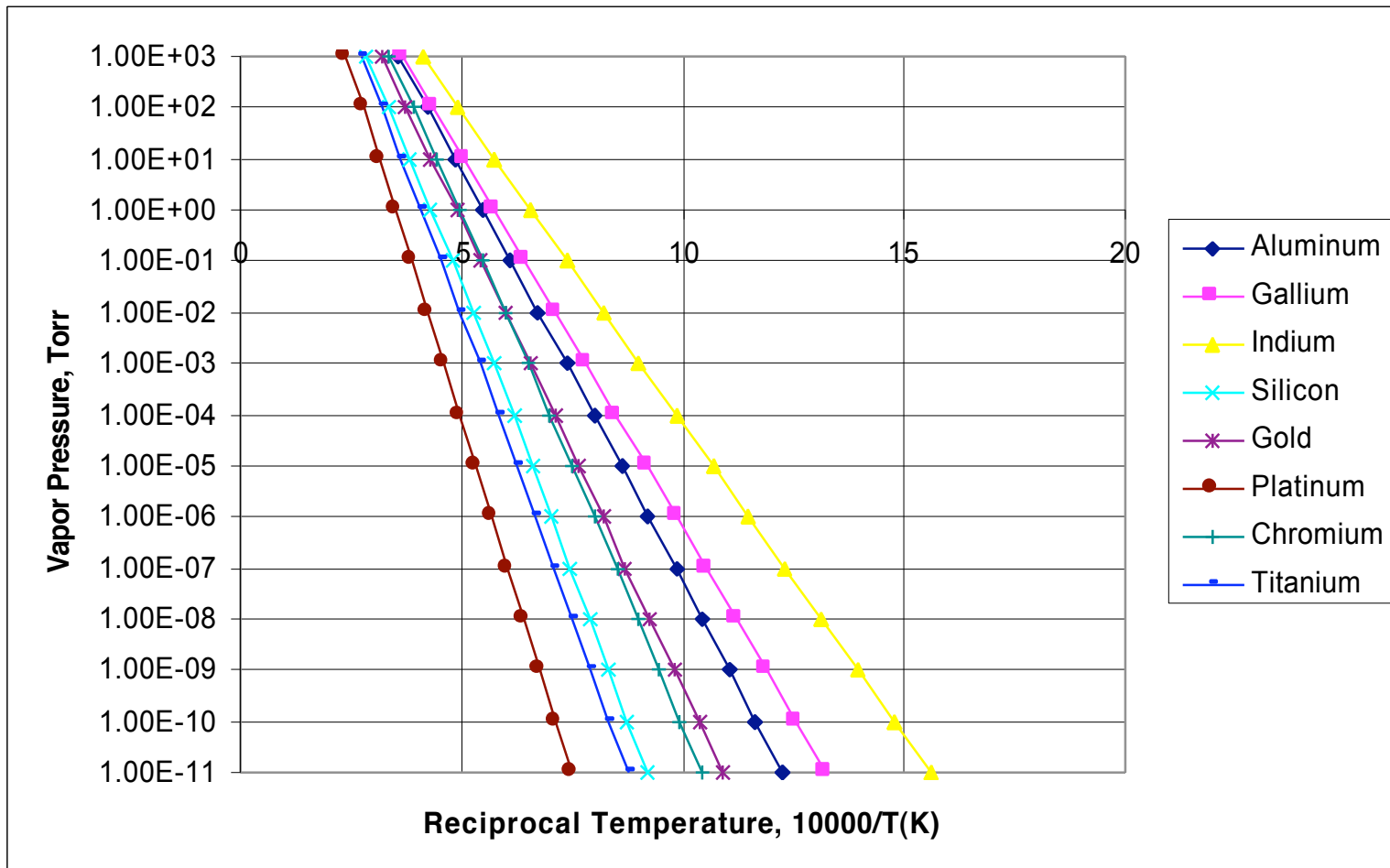
Evaporation System Requirements

- Vacuum:
  - Need 10^{-6} torr for medium quality films.
  - Can be accomplished in UHV down to 10^{-9} torr.

- Cooling water:
  - Hearth
  - Thickness monitor
  - Bell jar

- Mechanical shutter:
  - Evaporation rate is set by temperature of source, but this cannot be turned on and off rapidly. A mechanical shutter allows evaporant flux to be rapidly modulated.

- Electrical power:
 - Either high current or high voltage, typically 1-10 kW.

Evaporation Support Materials

- Refractory metals:
  - Tungsten (W); MP = 3380°C, P* = 10^{-2} torr at 3230°C
  - Tantalum (Ta); MP = 3000°C, P* = 10^{-2} torr at 3060°C
  - Molybdenum (Mo); MP = 2620°C, P* = 10^{-2} torr at 2530°C

- Refractory ceramics:
  - Graphitic Carbon (C); MP = 3700°C, P* = 10^{-2} torr at 2600°C
  - Alumina (Al_2O_3); MP = 2030°C, P* = 10^{-2} torr at 1900°C
  - Boron nitride (BN); MP = 2500°C, P* = 10^{-2} torr at 1600°C

- Engineering considerations:
  - Thermal conductivity
  - Thermal expansion
  - Electrical conductivity
  - Wettability and reactivity

Resistance Heated Evaporation

- Simple, robust, and in widespread use.
- Can only achieve temperatures of about 1800°C.
- Use W, Ta, or Mo filaments to heat evaporation source.
- Typical filament currents are 200-300 Amperes.
- Exposes substrates to visible and IR radiation.
- Typical deposition rates are 1-20 Angstroms/second.
- Common evaporant materials:
  - Au, Ag, Al, Sn, Cr, Sb, Ge, In, Mg, Ga
  - CdS, PbS, CdSe, NaCl, KCl, AgCl, MgF_2, CaF_2, $PbCl_2$

Resistance Heated Evaporation Sources
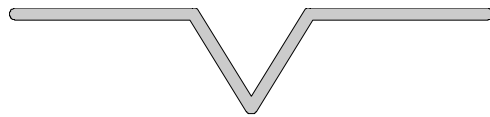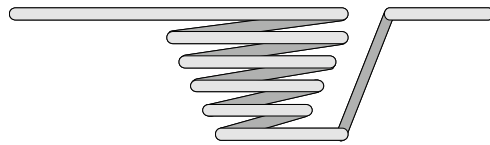
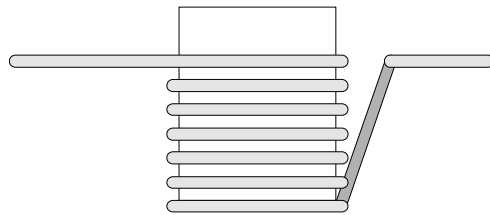wire hairpin

foil dimple boat

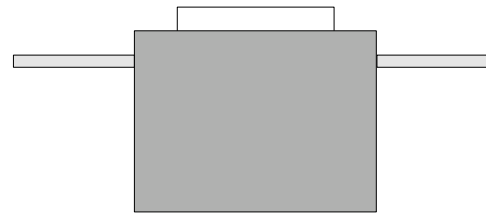wire helix

alumina coated foil dimple boat

foil trough

wire basket

chromium coated tungsten rod

alumina crucible with wire basket

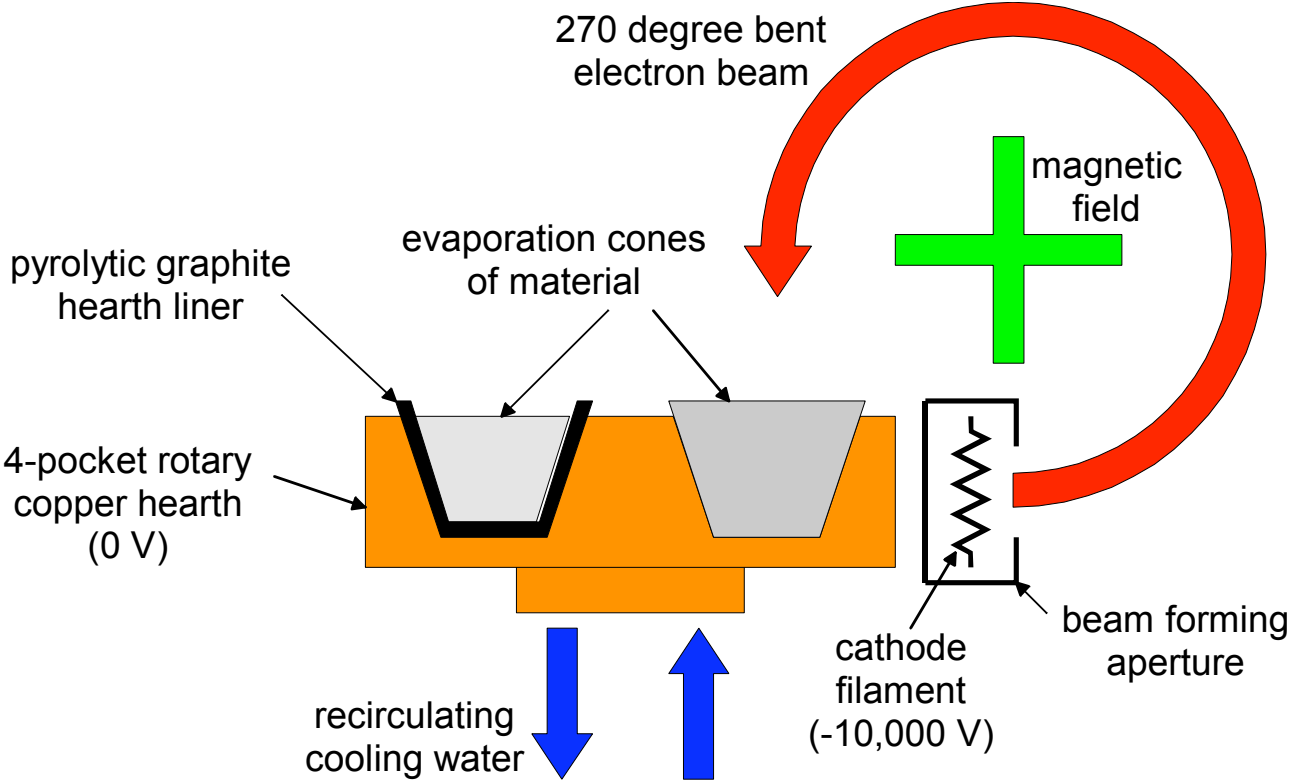alumina crucible in tantalum box

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Electron Beam Heated Evaporation - 1

- More complex, but extremely versatile.
- Can achieve temperatures in excess of 3000°C.
- Use evaporation cones or crucibles in a copper hearth.
- Typical emission voltage is 8-10 kV.
- Exposes substrates to secondary electron radiation.
  - X-rays can also be generated by high voltage electron beam.
- Typical deposition rates are 10-100 Angstroms/second.
- Common evaporant materials:
  - Everything a resistance heated evaporator will accommodate, plus:
  - Ni, Pt, Ir, Rh, Ti, V, Zr, W, Ta, Mo
  - Al_2O_3, SiO, SiO_2, SnO_2, TiO_2, ZrO_2

Electron Beam Heated Evaporation Source

270 degree bent
electron beam

magnetic
field

evaporation cones
of material

pyrolytic graphite
hearth liner

4-pocket rotary
copper hearth
(0 V)

recirculating
cooling water

cathode
filament
(-10,000 V)

beam forming
aperture

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Electron Beam Heated Evaporation - 2

- 270° bent beam electron gun is most preferred:
  - Filament is out of direct exposure from evaporant flux.
  - Magnetic field can be used for beam focusing.
  - Magnetic field can be used for beam positioning.
  - Additional lateral magnetic field can be used produce X-Y sweep.
- Sweeping or rastering of the evaporant source is useful for:
  - Allows a larger evaporant surface area for higher deposition rates.
  - Allows initial charge to be "soaked" or preheated.
  - Allows evaporant source to be more fully utilized.
- Multiple pocket rotary hearth is also preferred:
  - Allows sequential deposition of layers with a single pump-down.
  - Allows larger evaporation sources to be used.

High Throughput Evaporation Techniques

- Box coaters are used for evaporating large substrate materials, often up to several meters in size.

- Large amounts of source material are required, but cannot be all heated at once because of realistic power limitations.

- Two popular techniques:
  - Powder trickler source
  - Wire feed source

- Both can be adapted for either resistance heated or electron beam heated evaporation systems.

Adsorption

- Adsorption is the sticking of a particle to a surface.
- Physisorption:
  - The impinging molecule loses kinetic (thermal) energy within some residence time, and the lower energy of the molecule does not allow it to overcome the threshold that is needed to escape.

- Chemisorption:
  - The impinging molecule loses its kinetic energy to a chemical reaction which forms a chemical bond between it and other substrate atoms.

Condensation of Evaporant - 1

- Condensation of a vapor to a solid or liquid occurs when the partial pressure of the vapor exceeds the equilibrium vapor pressure of the condensed phase at this temperature.

- The vapor is "supersaturated" under these conditions.

- This is only true if condensation takes place onto material which is of the same composition as the vapor.

- When a material is first deposited onto a substrate of a different composition, a third adsorbed phase must be included to describe the process.

Condensation of Evaporant - 2

- Molecules impinging upon a surface may:
  - Adsorb and permanently stick where they land (rare!).
  - Adsorb and permanently stick after diffusing around on the surface to find an appropriate site.
    - This can lead to physisorption or chemisorption.
  - Adsorb and then desorb after some residence time τ_a.
  - Immediately reflect off of the surface.

- Incident vapor molecules normally have a kinetic energy much higher than $k_B T$ of the substrate surface.

- Whether an atom or molecule will stick depends upon how well it can equilibrate with the substrate surface, decreasing its energy to the point where it will not subsequently desorb.

Condensation of Evaporant - 3

- Thermal accomodation coefficient:

$$\alpha_T = \frac{E_v - E_r}{E_v - E_s} = \frac{T_v - T_r}{T_v - T_s}$$

  - E_v, T_v = energy, temperature of impinging vapor molecules.
  - E_r, T_r = energy, temperature of resident vapor molecules;
    - (Those which have adsorbed, but have not permanently found a site.)
  - E_s, T_s = energy, temperature of substrate surface.

- If $\alpha_T < 1$, ($E_r > E_s$), then some fraction of the impinging molecules will desorb from the surface.

Condensation of Evaporant - 4

- Mean residence time for an adsorbed molecule:

$$\tau_a = \frac{1}{\upsilon_0} \exp\left(\frac{\Delta G_{des}}{k_B T} \right)$$

  - $\upsilon_0 = k_B T / h$ = vibrational frequency of adsorbed molecule ($\sim 10^{14}$ Hz)
    - This is the frequency at which the molecule "attempts" to desorb.
  - ΔG_{des} = free activation energy for desorption.

- Under a constant impinging vapor flux of R, the surface density of the deposit is then:

$$n_s = R\tau_a = \frac{R}{\upsilon_0} \exp\left(\frac{\Delta G_{des}}{k_B T} \right)$$

  - R = deposition rate in molecules/cm²-sec.
  - n_s = surface density of deposited molecules in cm^{-2}.

Condensation of Evaporant - 5

- If the impingement rate stops, then the adsorbed molecules will all eventually desorb.

- Condensation of a permanent deposit will not occur, even for low substrate temperatures, unless the molecules interact.

- Within the mean residence time, surface migration occurs and clusters form.

- Clusters have smaller surface-to-volume ratios, and therefore desorb at a reduced rate.

- Nucleation of a permanent deposit is therefore dependent upon clustering of the adsorbed molecules.

Observed Growth of a Deposited Film

- Adsorbed monomers
- Subcritical embryos of various sizes
- Formation of critically sized nuclei
- Growth of nuclei to supercritical size and depletion of monomers within their capture zones
- Nucleation of critical clusters within non-depleted areas
- Clusters touch and coalesce into new islands, exposing fresh substrate areas
- Adsorption of monomers onto fresh areas
- Larger islands grow together leaving holes and channels
- Channels and holes fill to form a continuous film

Stages of Thin Film Growth

- Island Stage
- Coalescence Stage
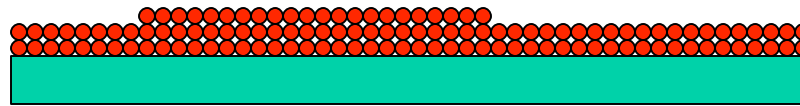- Channel Stage
- Continuous Film Stage

Modes of Thin Film Growth
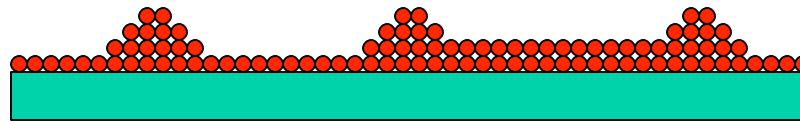
(1) Volmer-Weber: (island growth):
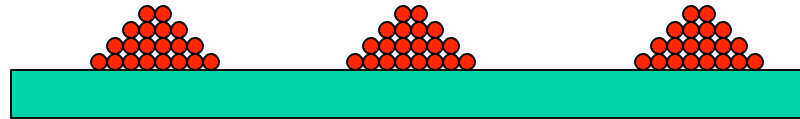
M. Volmer and A. Weber, *Z. Phys. Chem.* **119**, p. 277 (1926).

(2) Frank-Van der Merwe: (layer growth; ideal epitaxy):

F. C. Frank and J. H. Van der Merwe, *Proc. R. Soc. London*, Ser. A **198**, p. 205 (1949).

(3) Stranski-Krastanov: (layers + islands):

J. N. Stranski and L. Krastanov, *Ber. Akad. Wiss. Wien* **146**, p. 797 (1938).

Condensation Control

- Control of condensation of the evaporant is achieved through the control of substrate temperature T_s.

- Higher substrate temperatures:
  - Increase thermal energy of adsorbed molecules.
    - (Shortens the residence time.)
  - Increase surface diffusivity of adsorbed molecules.
  - Performs annealing of deposited film.

- Substrate heaters:
  - Quartz IR lamps from frontside
  - Ta, W, or Mo foil heaters from backside
  - Graphite impregnated cloth heaters from backside

- Too much heat will desorb the deposited film, evaporating it away! (But this can be used for cleaning…) R. B. Darling / EE-527