Thermodynamics

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ENTROPY

energy | space | matter | charge

temperature | pressure | chemical potential | electric potential

Classify systems according to how they interact with the rest of the world

	Exchange space	Exchange energy	Exchange matter
Open system	yes	yes	yes
Isolated system	no	no	no
Closed system	yes	yes	no
Thermal system	no	yes	no

Principles (Clausius 1865)

- An isolated system maximizes entropy.
- An isolated system conserves energy, space, matter, charge.

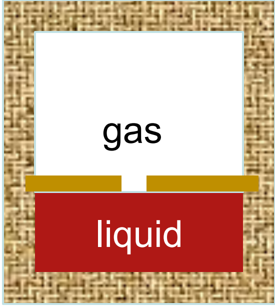
Entropy (Boltzmann 1877)

- An isolated system has a certain **number of microstates**.
- The isolated system flips from one microstate to another, rapidly and ceaselessly.
- The system isolated for a long time flips to every one of its microstate with equal probability.

- Entropy = k log (number of microstates)

- The function log makes entropy additive.
- The value of k is inconsequential.
- Some people set k = 1.
- Most other people follow another convention:
- Boltzmann constant k = 1.38 x 10^{-23} Joule/Kelvin.
- Such a silly way to honor three great scientists!

Algorithm

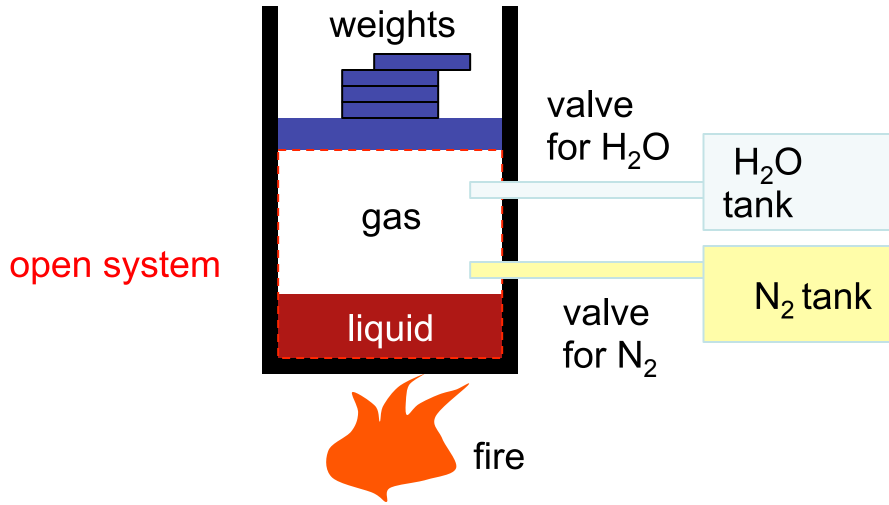


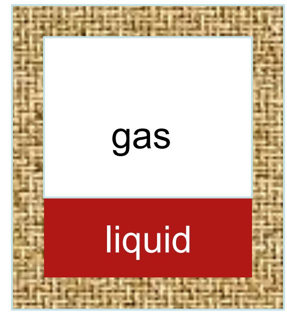
- (entropy) = log (number of microstates).
- Entropy is additive.

- When a **constraint internal to an isolated system** fixes an **internal variable** at a value *x*, the isolated system flips in a **subset** of microstates.
- Let the number of microstates in the subset be W(*x*).
- Call *S*(*x*) = log W(*x*) the entropy of the **configuration** of the isolated system when the internal variable is fixed at *x*.

1. Construct an **isolated system** with an **internal variable**, *x*.
2. When the internal variable is **constrained** at *x*, the isolated system has entropy *S*(*x*).
3. After the constraint is lifted, *x* changes to **maximize** *S*(*x*).

Model an open system as a family of isolated systems



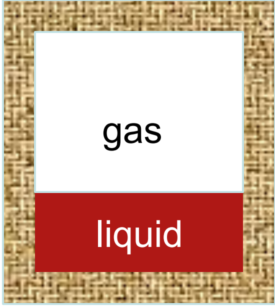


a family of isolated systems of four independent variables:
U, V, N_{H2O}, N_{N2}

- The wine contains **many components** (species of molecules) and **two phases**.
- The wine is an **open system**, exchanging energy, space, and **two** components with the rest of the world.
- Make the wine an **isolated system** by insulating the bottle, jam the piston, and shut the valves.
- A system isolated for a long time reaches a **state of thermodynamic equilibrium**.
- Define the entropy of the isolated system: $S = \log$ (number of microstates).
- Isolating the wine at various values of (U,V, N_{H2O}, N_{N2}), we obtain **a family of isolated systems** of **four** independent variables.
- Model the family of isolated systems by function $\mathbf{S(U,V, N_{H2O}, N_{N2})}$.

Derivative

1. an operation in calculus
2. a thing based on something else



a family of isolated systems
$S(U, V, N_A, N_B)$

Define temperature: $$\frac{\partial S(U,V,N_A,N_B)}{\partial U} = \frac{1}{T}$$

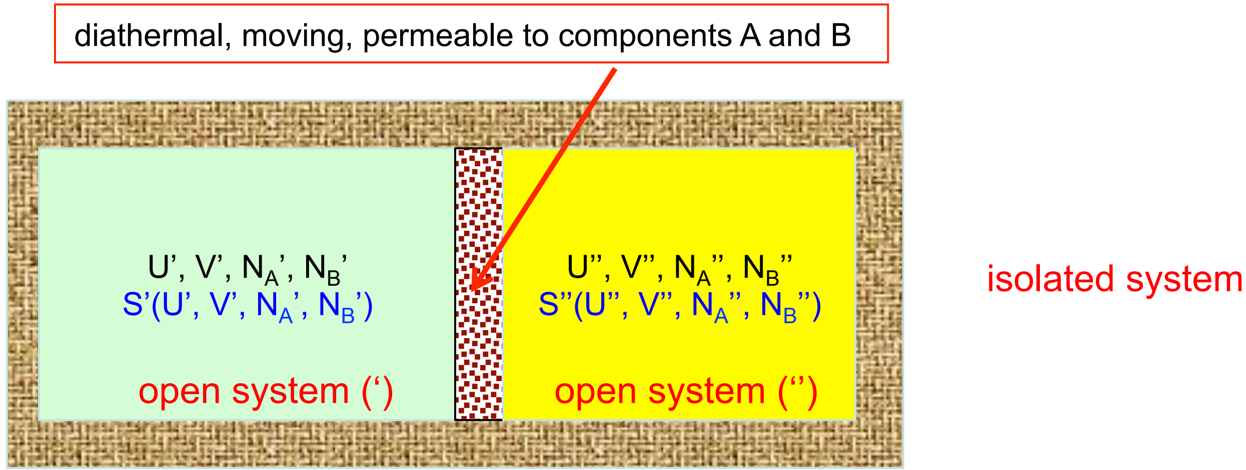
Define pressure: $$\frac{\partial S(U,V,N_A,N_B)}{\partial V} = \frac{P}{T}$$

Define chemical potential: $$\frac{\partial S(U,V,N_A,N_B)}{\partial N_A} = -\frac{\mu_A}{T}$$

Define chemical potential $$\frac{\partial S(U,V,N_A,N_B)}{\partial N_B} = -\frac{\mu_B}{T}$$

Calculus: $$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu_A}{T}dN_A - \frac{\mu_B}{T}dN_B$$

Two systems exchange energy, space, and molecules



Isolated system conserves energy, space, and matter over time:

$dU' + dU'' = 0.$

$dV' + dV'' = 0$

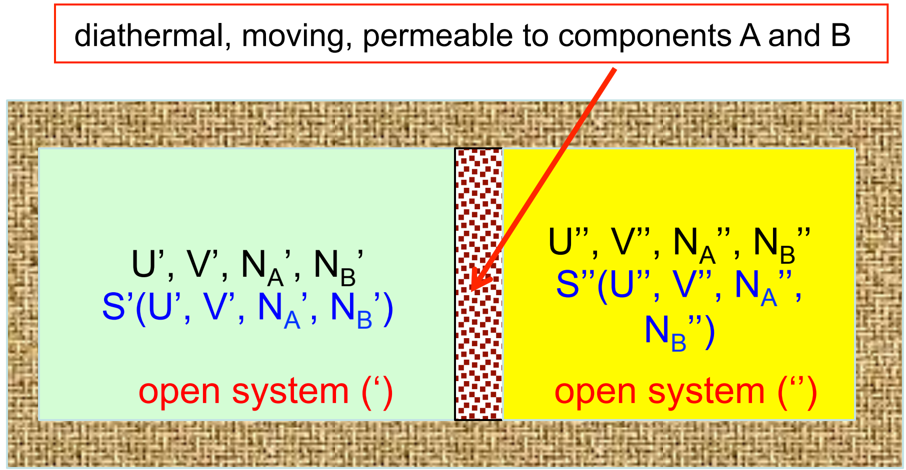
$dN_A' + dN_A'' = 0$

$dN_B' + dN_B'' = 0$

Isolated system **not in equilibrium** increases entropy over time: $dS' + dS'' > 0$

Isolated system **in equilibrium** keeps entropy constant over time: $dS' + dS'' = 0$

Equilibrating two systems



isolated system

$$d\left(S'+S''\right)=\left(\frac{1}{T'}dU'+\frac{P'}{T'}dV'-\frac{\mu'_A}{T'}dN'_A-\frac{\mu'_B}{T'}dN'_B\right)+\left(\frac{1}{T''}dU''+\frac{P''}{T''}dV''-\frac{\mu''_A}{T''}dN''_A-\frac{\mu''_B}{T''}dN''_A\right)$$

$$=\left(\frac{1}{T'}-\frac{1}{T''}\right)dU'+\left(\frac{P'}{T'}-\frac{P''}{T''}\right)dV'-\left(\frac{\mu'_A}{T'}-\frac{\mu''_A}{T''}\right)dN'_A-\left(\frac{\mu'_B}{T'}-\frac{\mu''_B}{T''}\right)dN'_B$$

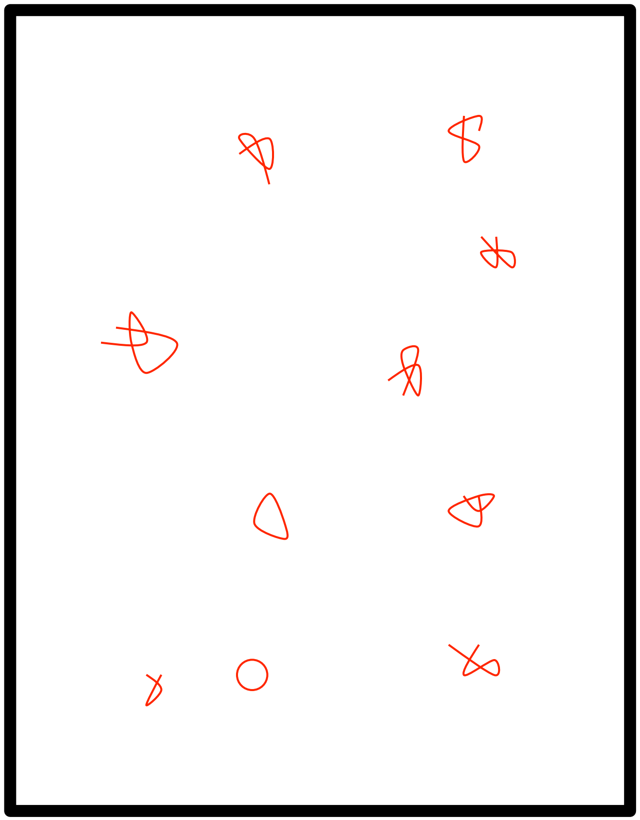
Thermal equilibrium: $T'=T''$

Mechanical equilibrium: $P'=P''$

Chemical equilibrium of component A: $\mu'_A=\mu''_A$

Chemical equilibrium of component B: $\mu'_B=\mu''_B$

Ideal gas



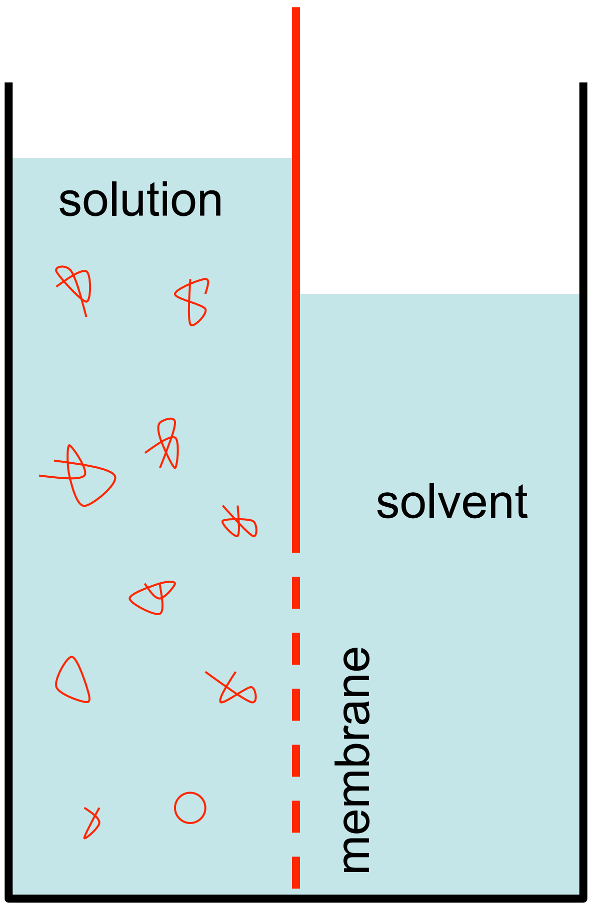
$$\left(\text{number of microstates}\right) \propto V^N$$

$$S = k \log V^N$$

$$P = T \frac{\partial S}{\partial V}$$

$$P = kT \frac{N}{V}$$

Osmosis



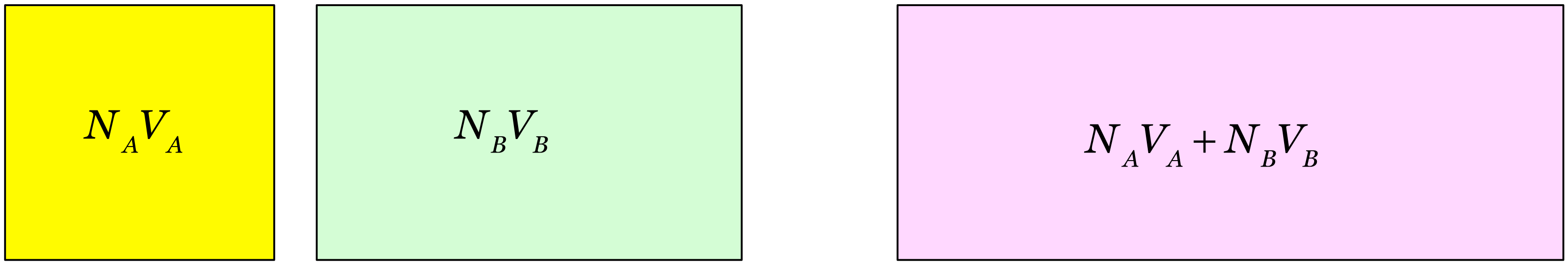
$$\left(\text{number of microstates}\right) \propto V^N$$

$$S = k \log V^N$$

$$P = T\frac{\partial S}{\partial V}$$

$$P = kT\frac{N}{V}$$

Ideal entropy of mixing



N_A = number of molecule A
V_A = volume per molecule A
$N_A V_A$ = volume of the sample

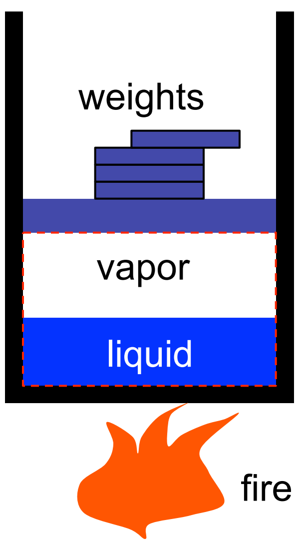
$$S_{\mathrm{mix}} = k \log \frac{\left(N_A V_A + N_B V_B\right)^{N_A + N_B}}{\left(N_A V_A\right)^{N_A} \left(N_B V_B\right)^{N_B}}$$

Huggins. J. Chem. Phys. 9, 440, 1941.
Flory. J. Chem. Phys. 10, 51, 1942.
This “derivation” can be found in Brassart, Liu, Suo. Journal of the Mechanics and Physics of Solids 96, 48 (2016)

Pure substance

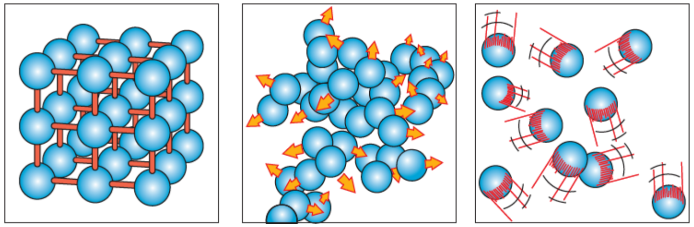
Count the number of microstates by experimental measurement

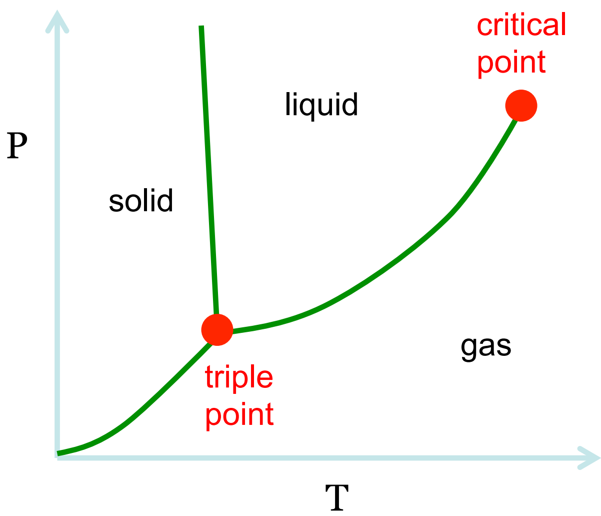
- Properties per molecule: $\bar{s} = \frac{S}{N}, \quad \bar{u} = \frac{U}{N}, \quad \bar{v} = \frac{V}{N}$
- Each pure substance has its own function $\bar{s}(\bar{u}, \bar{v})$
- Measure entropy incrementally. $d\bar{s} = \frac{1}{T}d\bar{u} + \frac{P}{T}d\bar{v}$

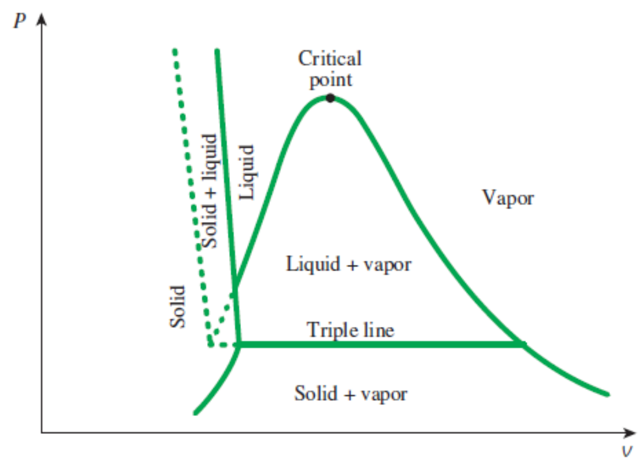


No quantum mechanics
No theory of probability
Just press and heat

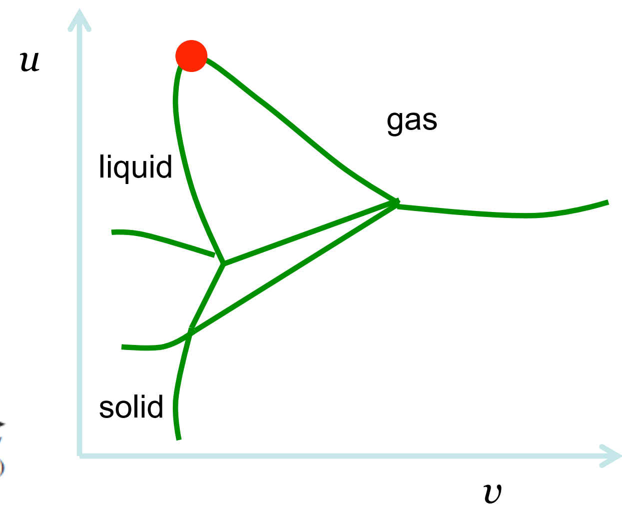
Three phases of a pure substance







(b) P-v diagram of a substance that expands on freezing (such as water)



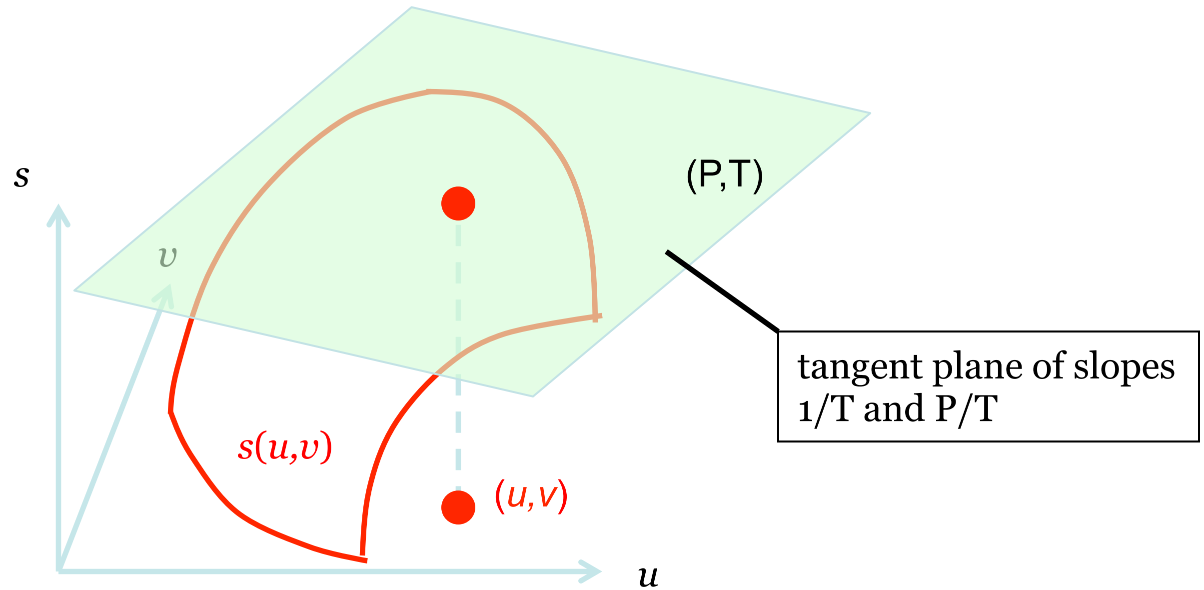
intensive-intensive extensive-intensive extensive-extensive

6 variables (PTvuhs), 15 choices of planes

A phase of a pure substance

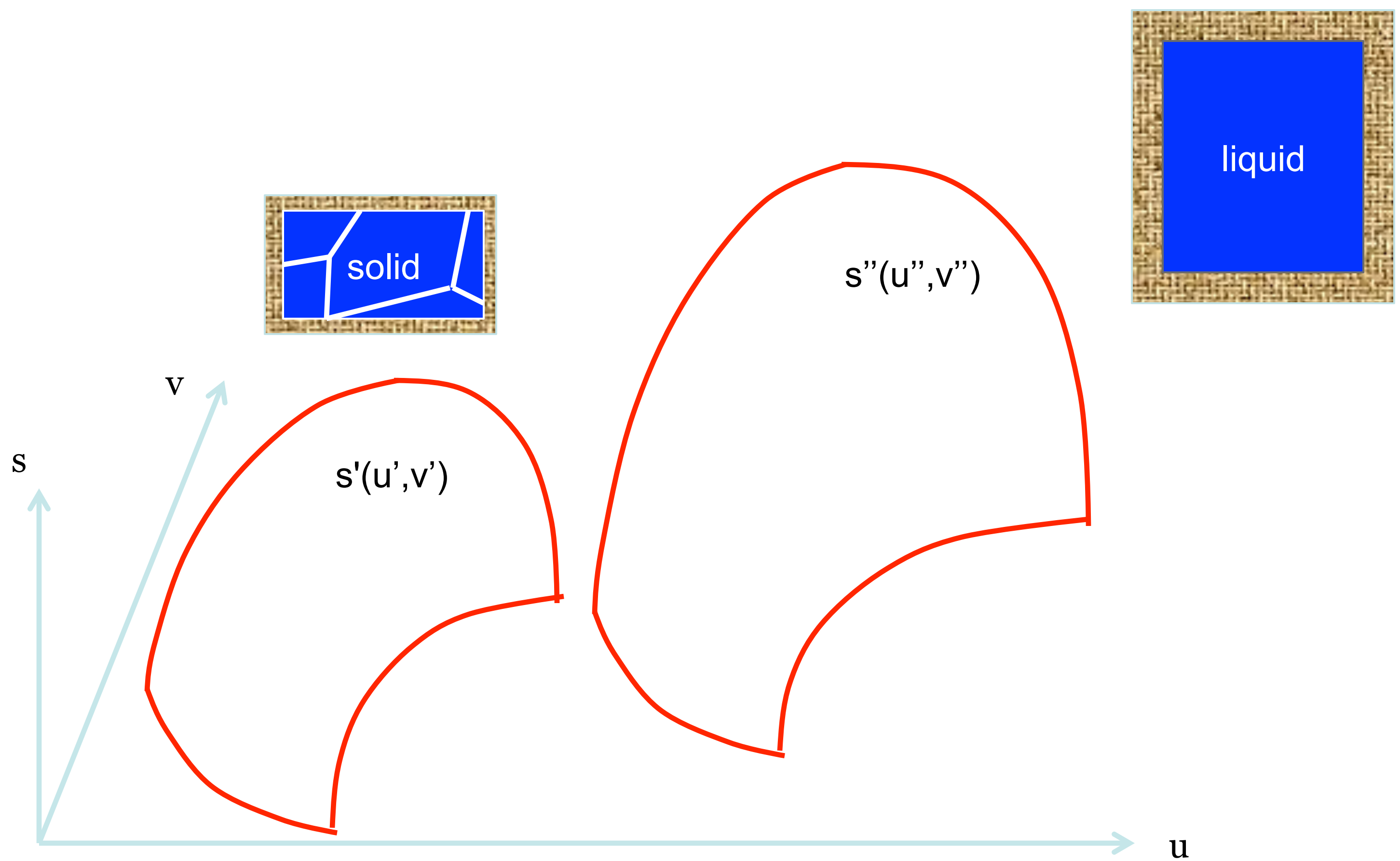
Gibbs relations $\frac{1}{T} = \frac{\partial s(u,v)}{\partial u}, \quad \frac{P}{T} = \frac{\partial s(u,v)}{\partial v}$

- s(u,v) is smooth and convex.
- Each tangent plane touches the surface at **a single point**.
- Roll the tangent plane with **two** degrees of freedom.
- point-to-point (P,T) ←→ (u,v).



Two co-existent phases of a pure substance

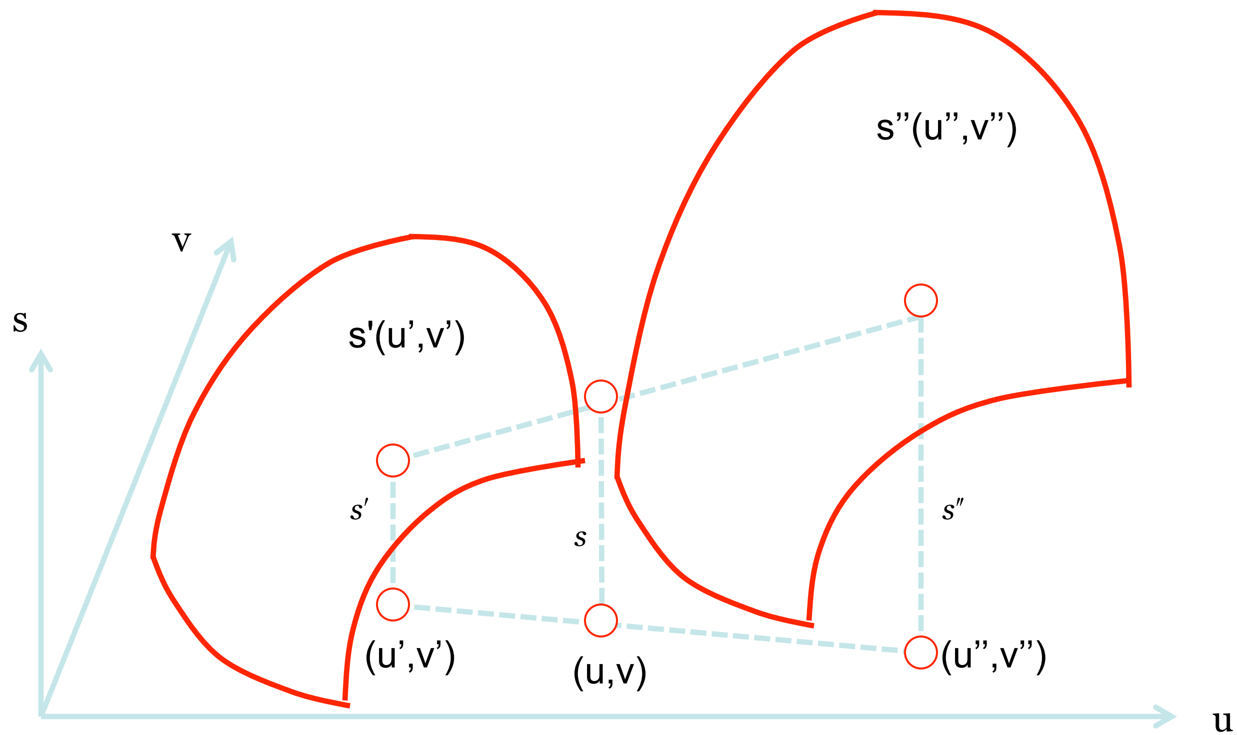
1. Each phase has its own smooth and convex s(u,v) function.

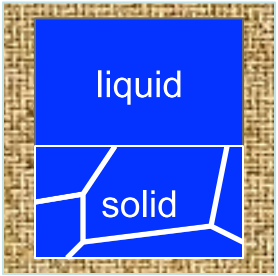


Two co-existent phases of a pure substance

2. Rule of mixture defines a line in the (s,u,v) space.

$$u = (1 - x)u' + xu''$$
$$v = (1 - x)v' + xv''$$
$$s = (1 - x)s' + xs''$$





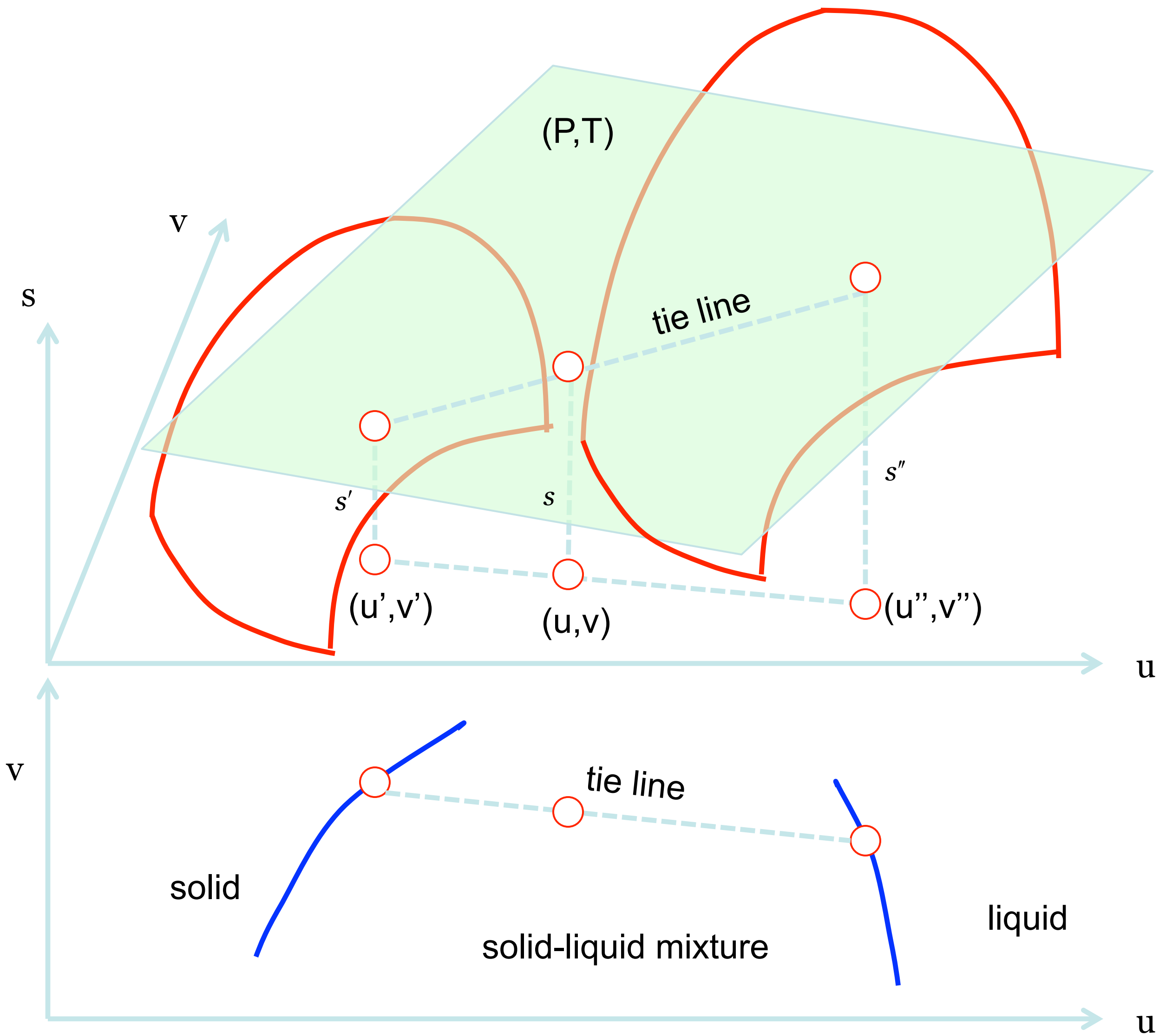
isolated system
of fixed u and v

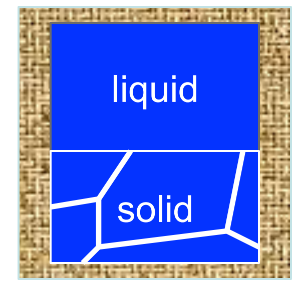
Two co-existent phases of a pure substance

3. Isolated system conserves energy and volume, but maximizes entropy.

Roll common tangent plane with one degree of freedom.

One-to-many correspondence: (P,T) ←→ (all states on the tie line)



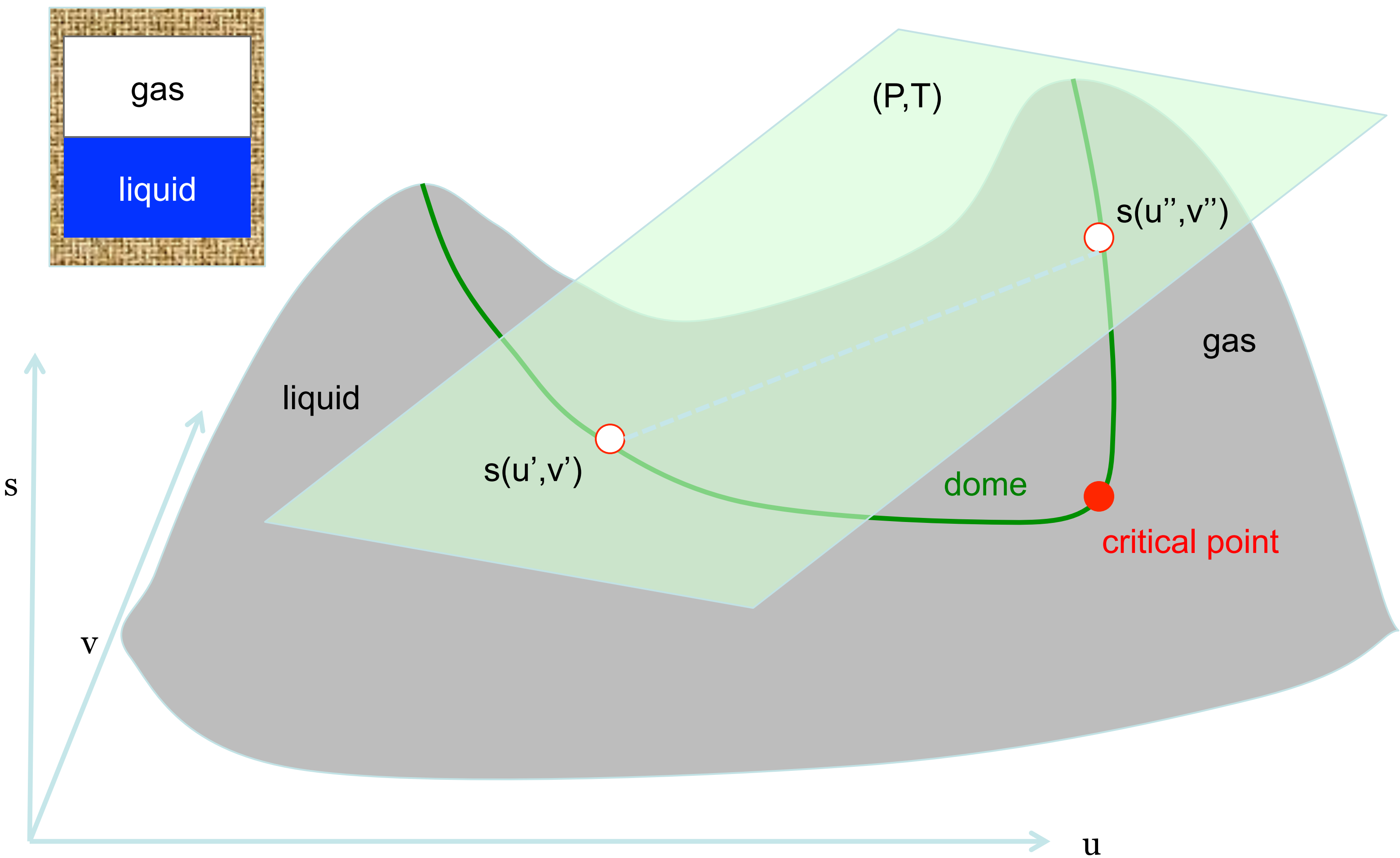


Two co-existent phases of a pure substance

4. Liquid and gas share a smooth but non-convex surface s(u,v)

Roll common tangent plane with one degree of freedom.

point-to-line (P,T) ←→ (u,v)



Three co-existent phases of a pure substance

Each phase has its own s(u,v) function. Common tangent plane cannot roll.

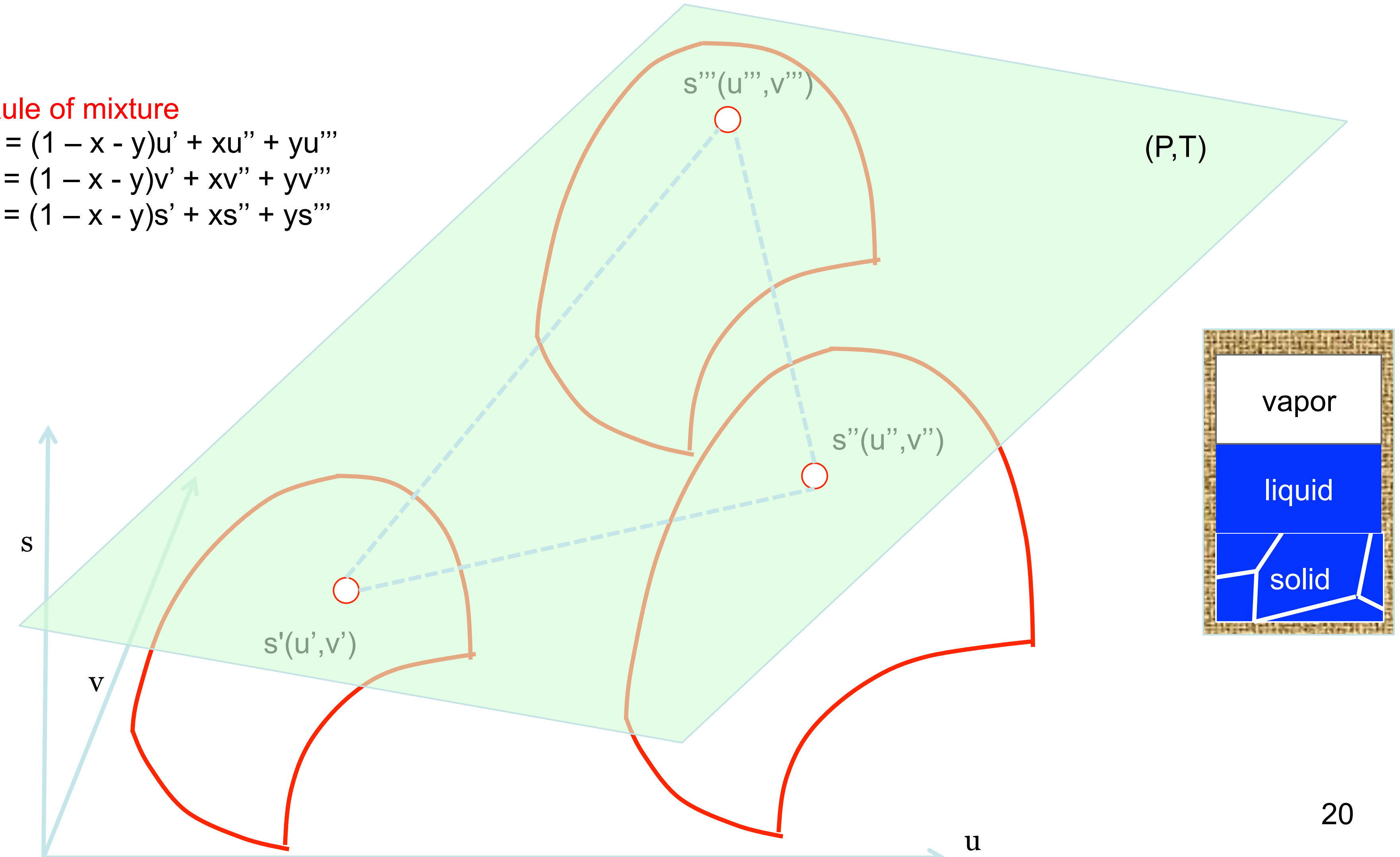
point-to-triangle (P,T) ←→ (u,v)

Rule of mixture

u = (1 – x - y)u' + xu'' + yu'''

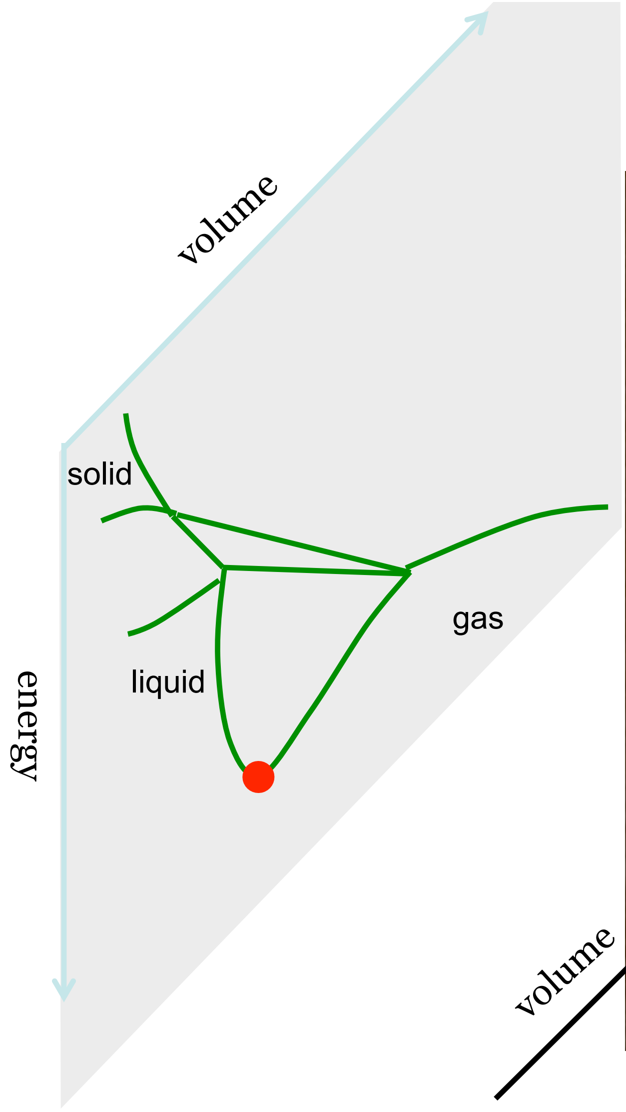
v = (1 – x - y)v' + xv'' + yv'''

s = (1 – x - y)s' + xs'' + ys'''



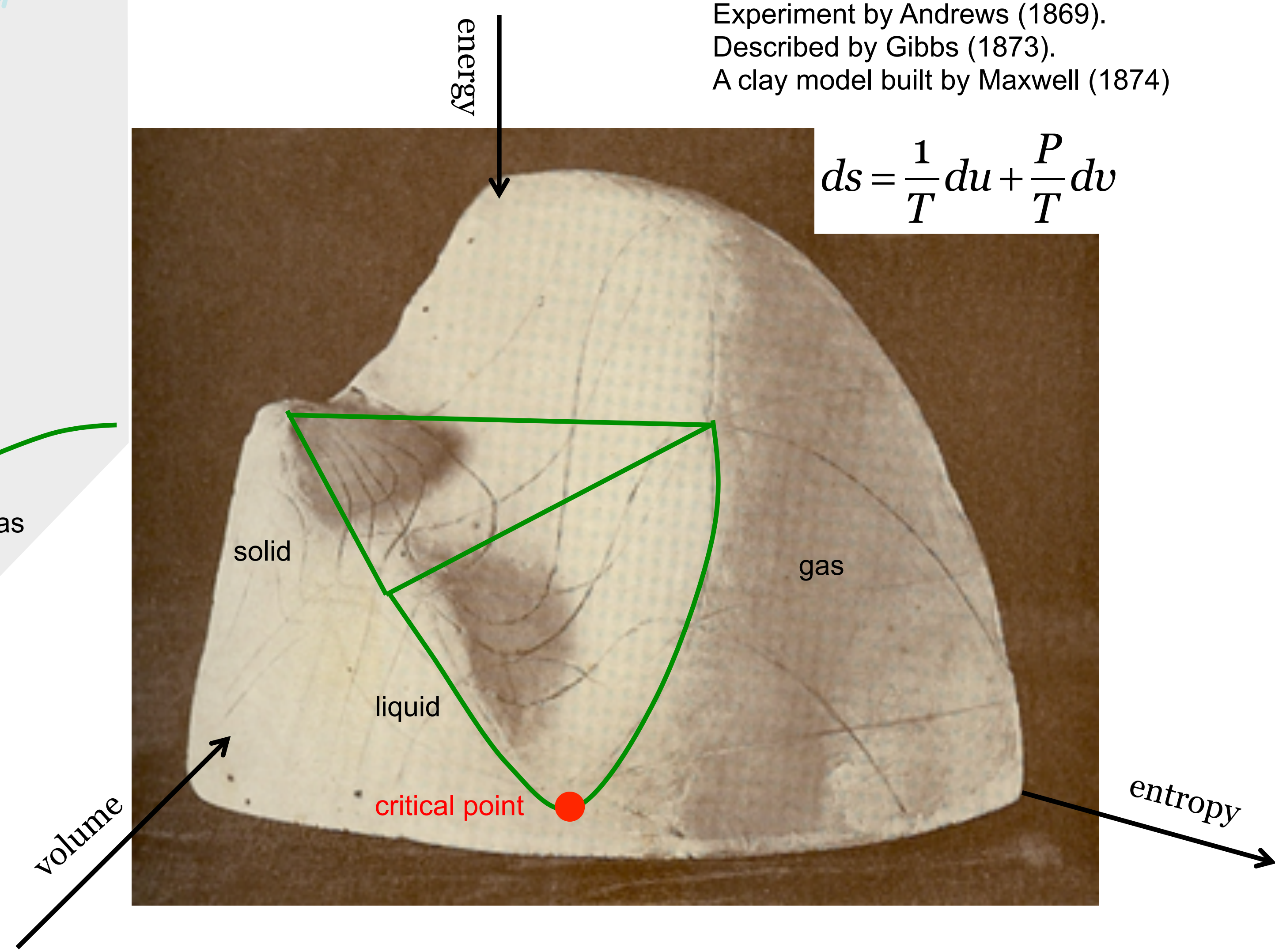
Gibbs's thermodynamic surface S(U,V)

Solid phase has its own smooth and convex s(u,v) function.
Liquid and gas phases share a smooth but non-convex s(u,v) function.
Use tangent planes to make s(u,v) surface convex (**convexification**)



Experiment by Andrews (1869).
Described by Gibbs (1873).
A clay model built by Maxwell (1874)

$$ds = \frac{1}{T}du + \frac{P}{T}dv$$



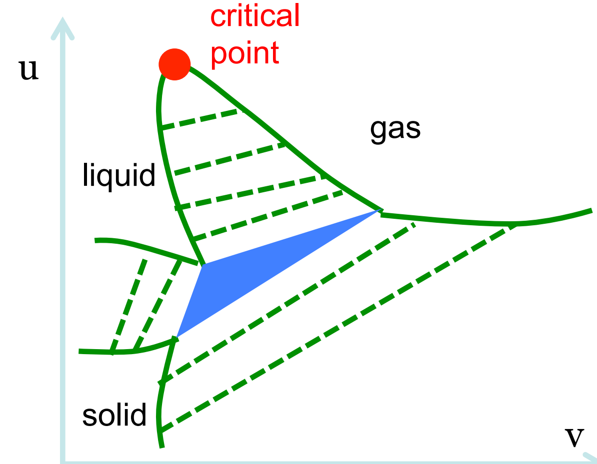
Gibbs's phase rule for a pure substance

Values of (P,T) give the slopes of a plane tangent to s(u,v) surface

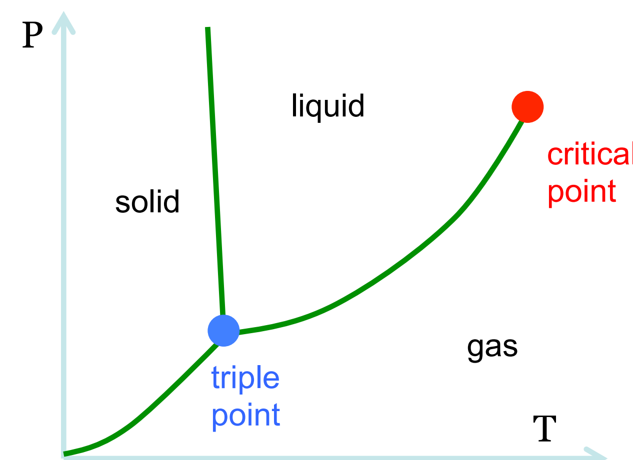
Single phase
- The tangent plane touches the s(u,v) surface of a single phase.
- Roll the tangent plane with two degrees of freedom.
- T and P change independently.
- A single phase corresponds to a **region** in the T-P plane.
- point-to-point (P,T) ←→ (u,v)

Two coexistent phases
- The tangent plane touches the s(u,v) surfaces of two phases.
- Roll the tangent plane with one degree of freedom.
- T depends on P.
- Two coexistent phases correspond to a **curve** in the T-P plane. **Phase boundary**.
- point-to-line (P,T) ←→ (u,v)

Three coexistent phases
- The tangent plane touches the s(u,v) surfaces of three phases.
- The tangent plane cannot roll.
- T and P are fixed.
- Three coexistent phases correspond to a **point** in the T-P plane. **Triple point**.
- point-to-triangle (P,T) ←→ (u,v)



extensive-extensive



Intensive-intensive

Water
P(T,s)
h(T,s)
r(T,s)
x(T,s)

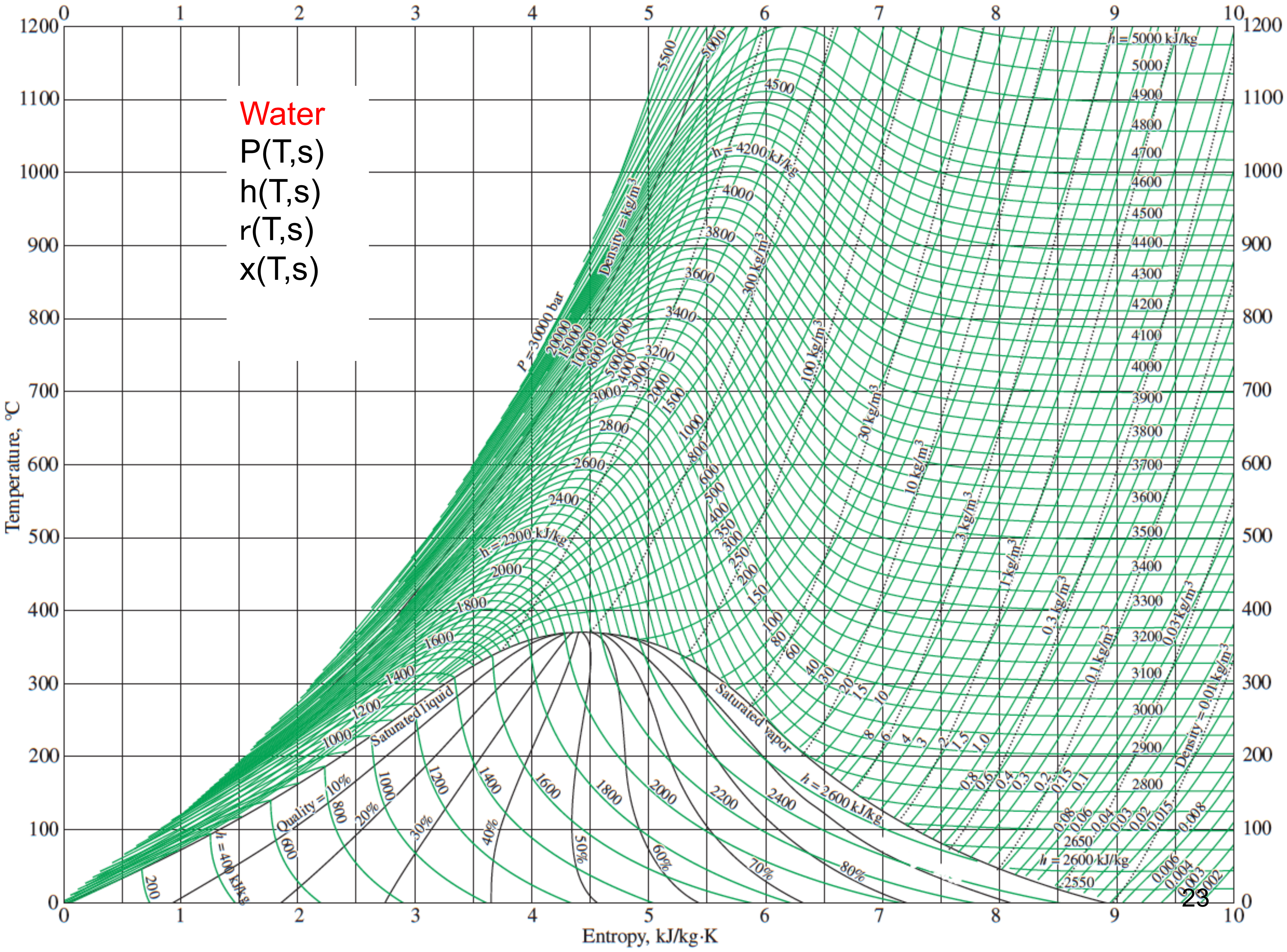


TABLE A–4

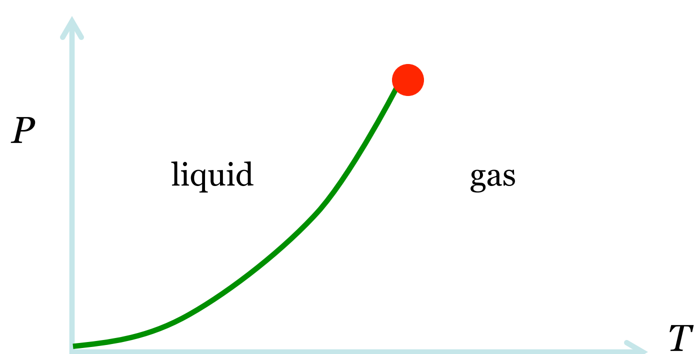
Saturated water—Temperature table

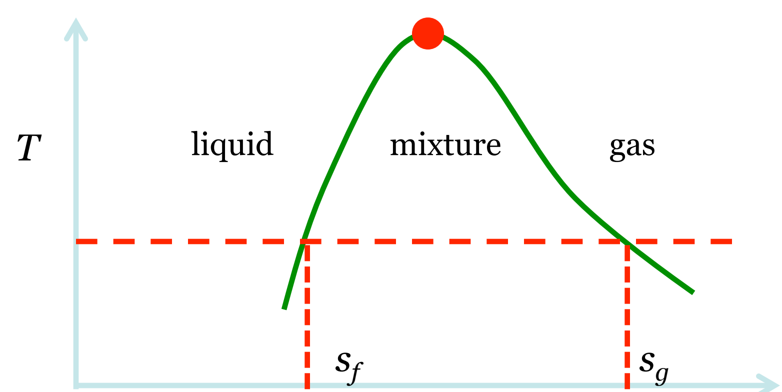
Temp., T °C	Sat. press., P_{sat} kPa	Specific volume, m³/kg: Sat. liquid, v_f	Sat. vapor, v_g	Internal energy, kJ/kg: Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Enthalpy, kJ/kg: Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Entropy, kJ/kg·K: Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.01	0.6117	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.019	2360.8	2381.8	21.020	2489.1	2510.1	0.0763	8.9487	9.0249
10	1.2281	0.001000	106.32	42.020	2346.6	2388.7	42.022	2477.2	2519.2	0.1511	8.7488	8.8999

TABLE A–6

Superheated water

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 0.01 MPa (45.81°C)*				P = 0.05 MPa (81.32°C)				P = 0.10 MPa (99.61°C)			
Sat.†	14.670	2437.2	2583.9	8.1488	3.2403	2483.2	2645.2	7.5931	1.6941	2505.6	2675.0	7.3589
50	14.867	2443.3	2592.0	8.1741								
100	17.196	2515.5	2687.5	8.4489	3.4187	2511.5	2682.4	7.6953	1.6959	2506.2	2675.8	7.3611
150	19.513	2587.9	2783.0	8.6893	3.8897	2585.7	2780.2	7.9413	1.9367	2582.9	2776.6	7.6148
200	21.826	2661.4	2879.6	8.9049	4.3562	2660.0	2877.8	8.1592	2.1724	2658.2	2875.5	7.8356

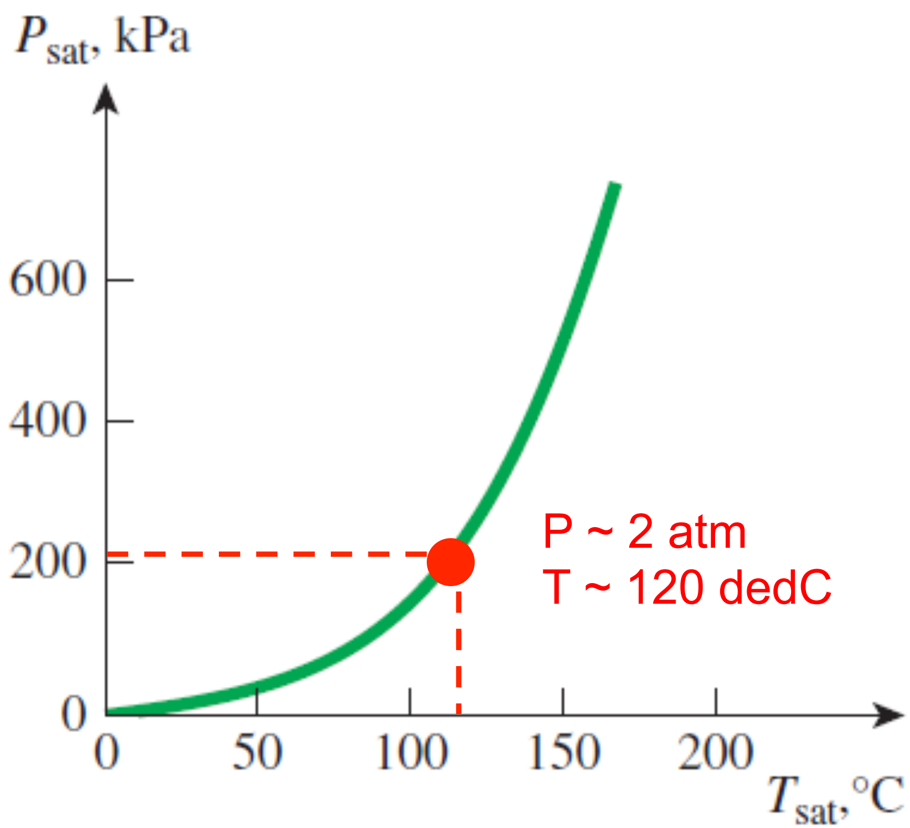


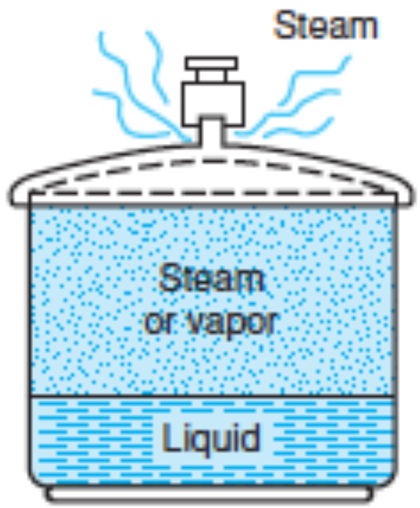


Pressure cooker

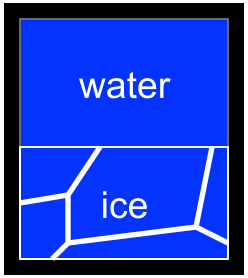
Invented by Denis Papin, France, 1679

Invention: increase pressure, increase temperature, reduce cooking time.
Science: When water and steam coexist, temperature increases with prresure.
Engineering: seal, strength, control pressure or temperature.



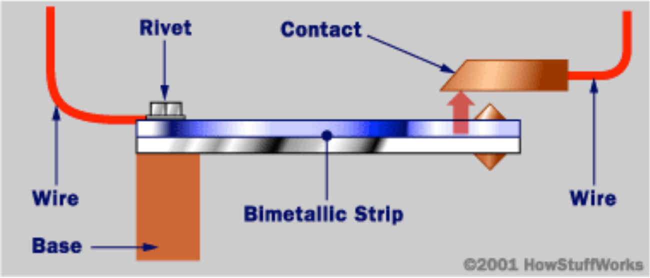


Experimental control of temperature



Ice-water mixture

thermal bath (heat reservoir)



thermostat

Thermodynamic model of reservoir of energy

- A reservoir of energy is a thermal system, and has a single independent variable, U_R.
- Entropy of the reservoir of energy is a thermodynamic property, $S_R(U_R)$.
- The reservoir of energy has a **fixed temperature**, T_R.

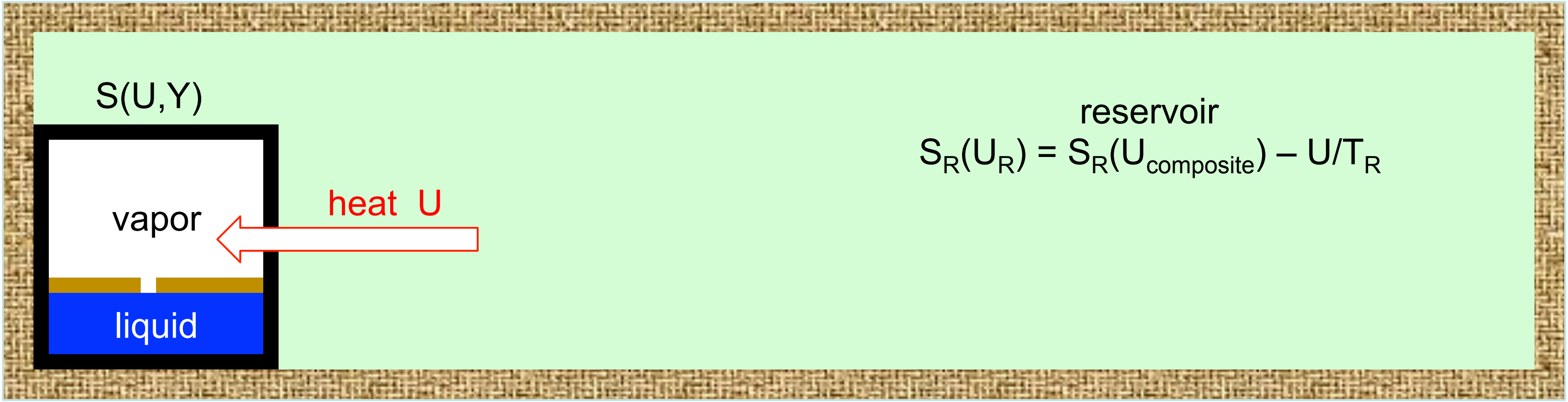
Clausius-Gibbs equation: $dS_R = \frac{dU_R}{T_R}$

Integration: $S_R(U_{R2}) - S_R(U_{R1}) = \frac{U_{R2} - U_{R1}}{T_R}$

Reservoir of water	Reservoir of energy
Potential energy PE	Internal energy U_R
Height h	Temperature T_R
Weight w	Entropy S_R
dPE = hdw	$dU_R = T_R dS_R$

Isothermal process

- (isolated system) = (small system) + (reservoir)
- Internal variables: the internal energy of the small system U, and something else Y
- Entropy is additive: $S_{\text{composite}} = S(U,Y) + S_R(U_{\text{composite}}) - \frac{U}{T_R}$
- Thermal equilibrium: $\frac{1}{T_R} = \frac{\partial S(U,Y)}{\partial U}$ $T_R = T$. $U(T,Y)$.
- At a fixed T, the internal variable Y changes to maximize $S(U,Y) - U/T$.
- Define the **Helmholtz free energy**: $F = U - TS$.
- At a fixed T, the internal variable Y changes to minimize $F(T,Y)$.



Breed equations (Gibbs 1878)

Gibbs equation: $$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu_A}{T}dN_A - \frac{\mu_B}{T}dN_B$$

Solve for dU: $$dU = TdS - PdV + \mu_A dN_A + \mu_B dN_B$$

Calculus:
$$T = \frac{\partial U\left(S,V,N_A,N_B\right)}{\partial S}$$
$$-P = \frac{\partial U\left(S,V,N_A,N_B\right)}{\partial V}$$
$$\mu_A = \frac{\partial U\left(S,V,N_A,N_B\right)}{\partial N_A}$$
$$\mu_B = \frac{\partial U\left(S,V,N_A,N_B\right)}{\partial N_B}$$

Helmholtz free energy

Gibbs equation: $$dU = TdS - PdV + \mu_A dN_A + \mu_B dN_B$$

Legendre transform defines the **Helmholtz function**: $$F = U - TS$$

Combine the above two equations: $$dF = -SdT - PdV + \mu_A dN_A + \mu_B dN_B$$

Calculus:

$$-S = \frac{\partial F(T,V,N_A,N_B)}{\partial T}$$

$$-P = \frac{\partial F(T,V,N_A,N_B)}{\partial V}$$

$$\mu_A = \frac{\partial F(T,V,N_A,N_B)}{\partial N_A}$$

$$\mu_B = \frac{\partial F(T,V,N_A,N_B)}{\partial N_B}$$

Gibbs free energy

Gibbs equation: $dU = TdS - PdV + \mu_A dN_A + \mu_B dN_B$

Legendre transform defines the **Gibbs function**: $G = U - TS + PV$

Combine the above two equations: $dG = -SdT + VdP + \mu_A dN_A + \mu_B dN_B$

Calculus:

$$-S = \frac{\partial G(T,P,N_A,N_B)}{\partial T}$$

$$V = \frac{\partial G(T,P,N_A,N_B)}{\partial P}$$

$$\mu_A = \frac{\partial G(T,P,N_A,N_B)}{\partial N_A}$$

$$\mu_B = \frac{\partial G(T,P,N_A,N_B)}{\partial N_B}$$

Chemical potentials

$$\frac{\partial S(U,V,N_A,N_B)}{\partial N_A} = -\frac{\mu_A}{T}$$

$$\frac{\partial S(U,V,N_A,N_B)}{\partial N_B} = -\frac{\mu_B}{T}$$

- These equations **define** the two chemical potentials.
- Each chemical potential is associated with a **component**.
- Chemical potential is an **intensive property**.
- T appears in the definition by convention.
- Negative sign appears in the definition by convention. Thus, an isolated system increases entropy when a component goes from a place of high chemical potential to a place of low chemical potential. (This statement will be made precise later.)
- Grammar: The chemical potential of a **component** in a **system** (e.g., chemical potential of water in the wine).

Chemical potential of a pure substance

Recall the definition of the Gibbs function per molecule (or per mole):

$$G(T,P,N) = N\bar{g}(T,P)$$

Recall the definition of chemical potential:

$$\mu = \frac{\partial G(T,P,N)}{\partial N}$$

Compare the two definitions:

$$\mu = \bar{g}(T,P)$$

Recall the definition of the Gibbs function:

$$\mu = \bar{g} = \bar{u} - T\bar{s} + P\bar{v}$$

Recall the Gibbs equation:

$$d\mu = -\bar{s}dT + \bar{v}dP$$

$$-\bar{s} = \frac{\partial \mu(T,P)}{\partial T}$$

$$\bar{v} = \frac{\partial \mu(T,P)}{\partial P}$$

1. For a pure substance, measure the function $\mu(T,P)$
2. Chemical potential requires the absolute entropy.
3. Chemical potential contains an arbitrary constant from energy.

Pure substance

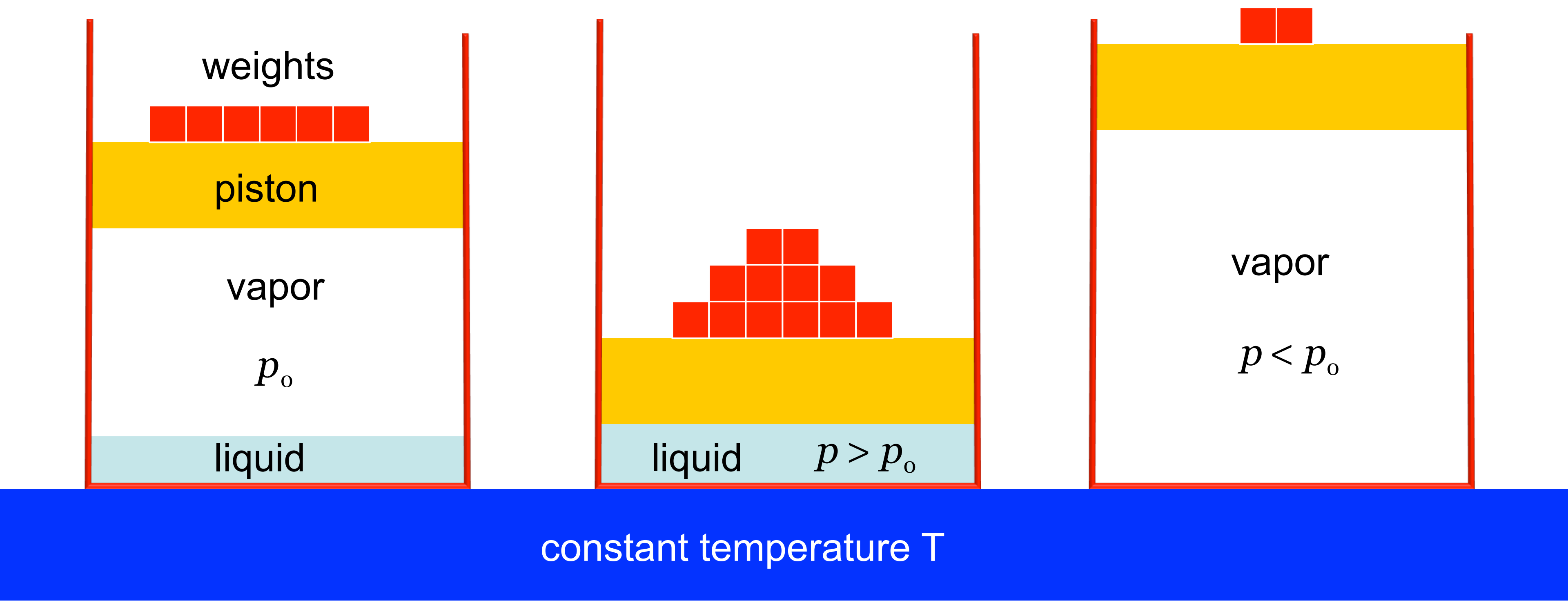
(an approximate model)

$$\bar{v} = \frac{\partial \mu(T,P)}{\partial P}$$

State of reference
liquid & vapor in equilibrium
$\mu = 0$

liquid only
$\mu = (p - p_o)\Omega$

vapor only
$\mu = kT \log(p/p_o)$
Relative humidity, p/p_o



p_o Pressure of saturated vapor

Ω volume per molecule

Measuring chemical potential of a **component** in a **system**

chemical potential of water in the wine

Chemical potential affects everything. Everything measures chemical potential