Agenda: TD of Dilute Gases, Simple Processes

- Fundamental ideal gas laws,
  - Equations of state (EoS)
  - Isothermal expansion/compression
  - Adiabatic expansion/compression
- Circular processes
  - Work, heat, and entropy in Carnot processes
  - Carnot, Kelvin/Clausius 2ndLTD
    - Thermodynamic driving potentials
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- Statistical Mechanics
  - Quantum statistics
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Weeks 7 & 8
LN IV.4-7:

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McQuarrie & Simon
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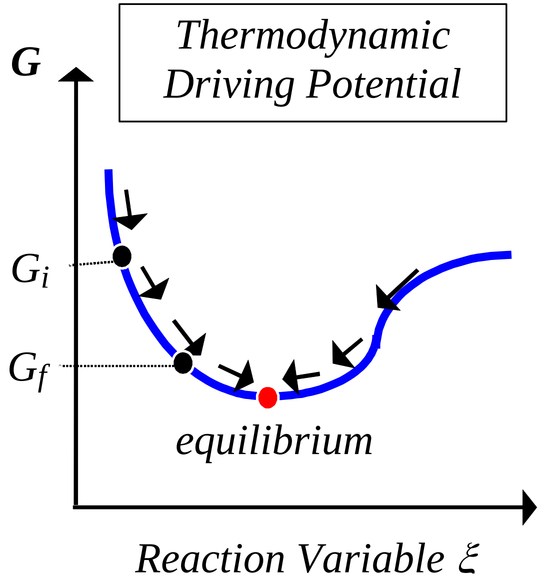
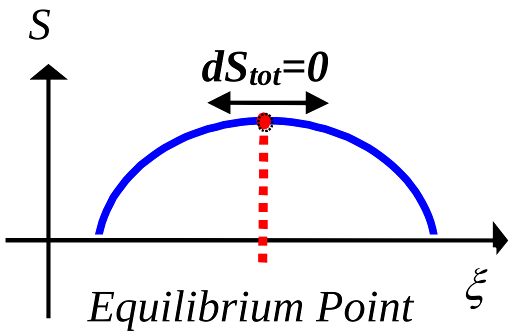
Reversible Work and Free Energy



Thermal Equilibrium

Stable Equilibrium



Maximum work a canonical system @ $S \leq S_{max}$ can perform spontaneously using thermal energy dq

$$\text{Net heat+ work changes}\begin{Bmatrix}\text{int. energy}\\ \text{enthalpy}\end{Bmatrix}\rightarrow\left\{(q+w)=\begin{matrix}dU\\ dH\end{matrix}\right\}$$

Helmholtz Free Energy

$$\boxed{A = U - T\cdot S}$$

***V, T* =const.**

Work in reversible processes

$$dU = q_{rev} + w_{rev} = T\cdot dS + w_{rev}$$

$$w_{rev} = dU - T\cdot dS = d\left(U - T\cdot S\right) = dA$$

Gibbs Free Energy

$$\boxed{G = H - T\cdot S}$$

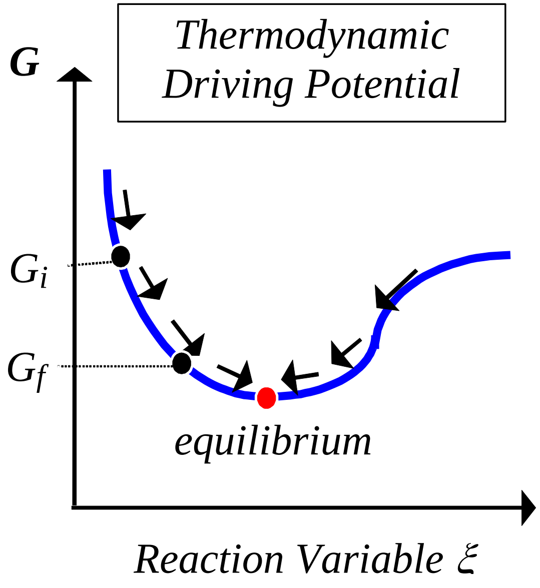
***P, T* =const.**

Work in reversible processes

$$dH = q_{rev} + w_{rev} = T\cdot dS + w_{rev}$$

$$w_{rev} = dH - T\cdot dS = d\left(H - T\cdot S\right) = dG$$

Reversible Work and Free Energy



Thermal Equilibrium

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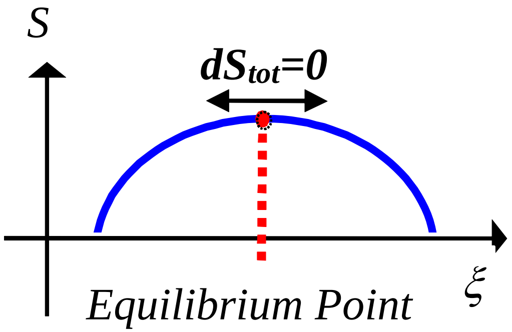


Maximum work by a canonical system @ S<S$_{max}$

Gibbs Free Energy $\boxed{G = H - T\cdot S}$ ***T* =const.**

***W*ork or *G* in reversible IG processes ?**

$w_{rev} = dH - T\cdot dS = d\left(H - T\cdot S\right) = dG$

$NOTE: dH \neq q_{rev}$
$since\ p \neq const$

$$\boxed{dG = d\left(U + p\cdot V\right) - d\left(T\cdot S\right)}$$

At **T = const**

$dG = dU + dp\cdot V + \underline{p\cdot dV} - \cancel{dT\cdot S}\ \underline{\underline{-T\cdot dS}}$

with $= q + w = \underline{\underline{T\cdot dS}} - \underline{p\cdot dV}$

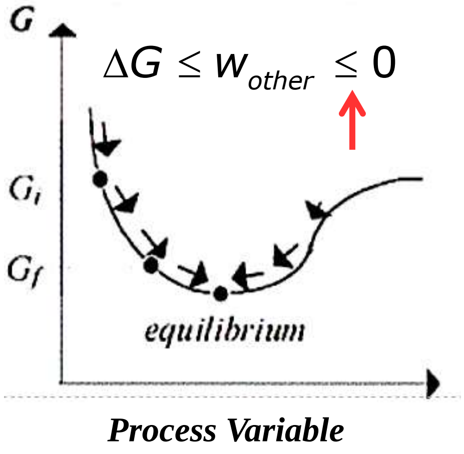
$\rightarrow dG\big|_T = dp\cdot V \rightarrow \boxed{\left(\frac{\partial G}{\partial p}\right)_T = V} \leftarrow p = dependence$

Work in isothermal reversible IG process

$$\boxed{w_{rev} = dG\big|_T = V\cdot dp}$$

Thermodynamic Energies & Driving Potentials

Potential energy gain in energetically allowed process (chem. rxn $\Delta H^0_{rxn} = H^0_{products} - H^0_{reagents} < 0$) *does not guarantee spontaneity* → $\boxed{\Delta S > 0\,?}$



$\Delta G \le w_{other} \le 0$ ↑

Helmholtz free energy $\boxed{A = U - T \cdot S \ \text{used @ const } V, T}$

System *will do spontaneously* : $w_{process} = \Delta A_{process} < 0$

Gibbs free energy $\boxed{G = H - T \cdot S \ \text{used @ const } p, T}$

System *will do spontaneously* : $w_{process} = \Delta G_{process} < 0$

Example : "extra" work a system can do beyond pV : $\boxed{w_{other} = \Delta G}$

Electrical potential Φ, *charge* e → $\boxed{work = e \cdot d\Phi}$

$dG = d\left(U + \underline{e \cdot \Phi} + p \cdot V\right) - d\left(T \cdot S\right)$ **(p, T = const)**

$dG = \cancel{dU} + \underline{d\left(e \cdot \Phi\right)} + \cancel{dp \cdot V} + \cancel{p \cdot dV} - \cancel{dT \cdot S} - \cancel{T \cdot dS}$

↳ $dU = heat + work\ on\ system = \cancel{T \cdot dS} - \cancel{p \cdot dV}$

Extra electrical work

$\boxed{dG = d\left(e \cdot \Phi\right) = w_{other}}$

Spontaneous if dG<0

Canonical Thermodynamic IG Entropy Connections

Differentials of state functions ***U, H, S, A, G, V, N*** ***T=const***

Ideal gas: $pV = Nk_BT$ *and* $\boldsymbol{U = (3/2)Nk_BT}$

General 1st. LTD any process $\boldsymbol{dU = dq - p\cdot dV + \mu\cdot dN + \ldots}$

Reversible processes → $\boldsymbol{dU = T\cdot dS - p\cdot dV + \mu\cdot dN + \ldots}$

$$dU(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N,\ldots} \cdot dS + \left(\frac{\partial U}{\partial V}\right)_{S,N,\ldots} \cdot dV + \left(\frac{\partial U}{\partial N}\right)_{S,V,,\ldots} \cdot dN + \ldots.$$

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p \qquad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu \ \ldots.$$

Set N=const
→ dN=0

Complete differential

$$dS = \frac{dU}{T} + \frac{p}{T}dV = \frac{3}{2}Nk_B\frac{dT}{T} + Nk_B\frac{dV}{V}$$

Integrate

$$S(T,V) = S_0(T_0,V_0) + Nk_B \cdot Ln\left\{\left(\frac{T}{T_0}\right)^{3/2} \cdot \left(\frac{V}{V_0}\right)\right\} = S_0(T_0,V_0) + Nk_B \cdot Ln\left\{\left(\frac{T}{T_0}\right)^{5/2} \cdot \left(\frac{p_0}{p}\right)\right\}$$

Since $V \propto 1/p$

Canonical Thermodynamic IG Entropy Connections

Differentials of state functions ***U, H, S, A, G, V, N*** ***T=const.***

Ideal gas: *$pV = Nk_BT$ and* **$U = (3/2)Nk_BT$** *per particle*

General 1st. LTD any process $\boldsymbol{dU = dq - p\cdot dV + \mu\cdot dN + \ldots}$

Reversible processes → $\boldsymbol{dU = T\cdot dS - p\cdot dV + \mu\cdot dN + \ldots}$

$$\boxed{S(T,V)=S_0(T_0,V_0)+Nk_B\cdot\ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\cdot\left(\frac{V}{V_0}\right)\right\}}=S_0(T_0,V_0)+Nk_B\cdot\ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\cdot\left(\frac{p_0}{p}\right)\right\}$$

⇓

Similarly

$$S(T,V,..)=\left(\frac{\partial S}{\partial T}\right)_V\cdot T+\left(\frac{\partial S}{\partial V}\right)_T\cdot V+\cdots$$

$$\left(\frac{\partial S}{\partial T}\right)_V=\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V=\frac{1}{T}C_V \qquad \left(\frac{\partial S}{\partial V}\right)_T=\frac{1}{T}\cancel{\left(\frac{\partial U}{\partial V}\right)_T}+\frac{1}{T}p=\frac{1}{T}p$$

$$S(V,T)=C_V+\frac{1}{T}p\cdot V=C_V+k_B=\frac{3}{2}k_B+k_B=\frac{5}{2}k_B \Rightarrow \boxed{S(V,T)=\frac{5}{2}k_B=C_P}$$

Thermodynamic Relations: Free Energy

$dA(V,T) = d(U - TS) = dU - SdT - TdS = (dq_{rev} - pdV) - SdT - TdS$

$\rightarrow dA(V,T) = -pdV - SdT$

$$dA(V,T) = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -p$$

$$dG(p,T,N) = Vdp - SdT + \mu \cdot dN = \left(\frac{\partial G}{\partial p}\right)_{T,N} \cdot dp + \left(\frac{\partial G}{\partial T}\right)_{p,N} \cdot dT + \left(\frac{\partial G}{\partial N}\right)_{p,T} \cdot dN$$

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = V \; \Big| \; \left(\frac{\partial G}{\partial T}\right)_{p,N} = -S \; \Big| \; \left(\frac{\partial G}{\partial N}\right)_{T,p} = \mu \; \Big|$$

Gibbs-Duhem relation

$$\boxed{d\mu = V \cdot dp - S \cdot dT}$$

$k_B T / p$

$$\boxed{d\mu = k_B T \cdot d\,Ln(p) - \left(s_0 k_B + k_B \cdot Ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\right\}\right) dT}$$

Thermodynamic Equilibrium State Functions

State Function	Fundamental Total Differential	@Equilibrium
$U(S,V,N)$	$dU=TdS-pdV+\Sigma_j\mu_j dN_j$ (mix, species j)	Minimum
$S(U,V,N)$	$dS=(1/T)dU+(p/T)dV-\Sigma_j(\mu_j/T)dN_j$	Maximum
$H(S,p,N)=U+pV$	$dH= TdS+Vdp+\Sigma_j\mu_j dN_j$	Minimum
$A(T,V,N)=U-TS$	$dA=-S\,dT-pdV+\Sigma_j\mu_j dN_j$	Minimum
$G(T,p,N)=H-TS$	$dG=-S\,dT+V\,dp+\Sigma_j\mu_j dN_j$	Minimum
Mixtures $N=\Sigma_j dN_j$		

Chemical potential per particle type i: $\mu_i = \left(\frac{dG}{dN_i}\right)_{p,T}$

For canonical ensembles @

V=const., N_i=const. $dU = TdS - \cancel{pdV} + \cancel{\sum_j \mu_j dN_j} \rightarrow dU = TdS$

P=const., N_i=const. $dH = TdS + \cancel{Vdp} + \cancel{\sum_j \mu_j dN_j} \rightarrow dH = TdS$

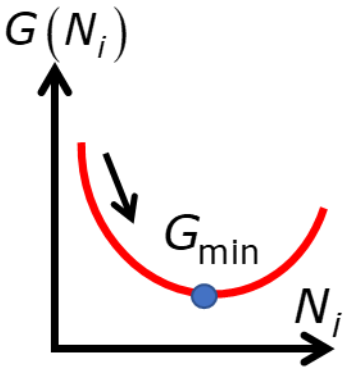
Reversible energy changes $dq = dU$ @ T,V and $dq = dH$ @ p,T

$$dS_{rev} = \frac{dq}{T}$$

Irreversible internal entropy changes (randomness)

$$dS_{irrev} > 0$$

Grand Canonical PF: Application to Reactions



cut through multi-dimensional energy surface

Generic chemical reaction in gas phase

$$\nu_A \cdot A + \nu_B \cdot B \rightleftharpoons \nu_C \cdot C + \nu_D \cdot D$$

$$\textit{Change in chemical potential } (@T) \to \mu_i = \left(\frac{\partial G}{\partial N_i}\right)$$

$$\Delta\mu = \nu_C \cdot \mu_C + \nu_D \cdot \mu_D - \nu_A \cdot \mu_A - \nu_B \cdot \mu_B$$

ν_i in moles

$$\boxed{\mu_i(p_i, T) = \mu_i^0(T) + R \cdot T \cdot Ln(p_i/p_0); \quad p_0 := 101kPa}$$

$$\Delta\mu = \Delta\mu^0 + R \cdot T \cdot Ln\left[\frac{(p_C)^{\nu_C}(p_D)^{\nu_D}}{(p_A)^{\nu_A}(p_B)^{\nu_B}}\right] \quad \textit{all relative to } p_0$$

For EoS $p \cdot V = n \cdot R \cdot T$

$R = 8.31446262\ J/K \cdot mol$

$$S = S_{max} \to \Delta\mu = 0 \to \boxed{\Delta\mu^0 = -R \cdot T \cdot Ln\left[\frac{(p_C)^{\nu_C}(p_D)^{\nu_D}}{(p_A)^{\nu_A}(p_B)^{\nu_B}}\right] = -RT \cdot Ln\, K_p}$$

Equilibrium Constant

$$\boxed{K_p = \left[\frac{(p_C)^{\nu_C}(p_D)^{\nu_D}}{(p_A)^{\nu_A}(p_B)^{\nu_B}}\right] = exp\left\{-\frac{\Delta\mu^0}{R \cdot T}\right\}}$$

Similar for
$p \to (n/V) = [\ ]$

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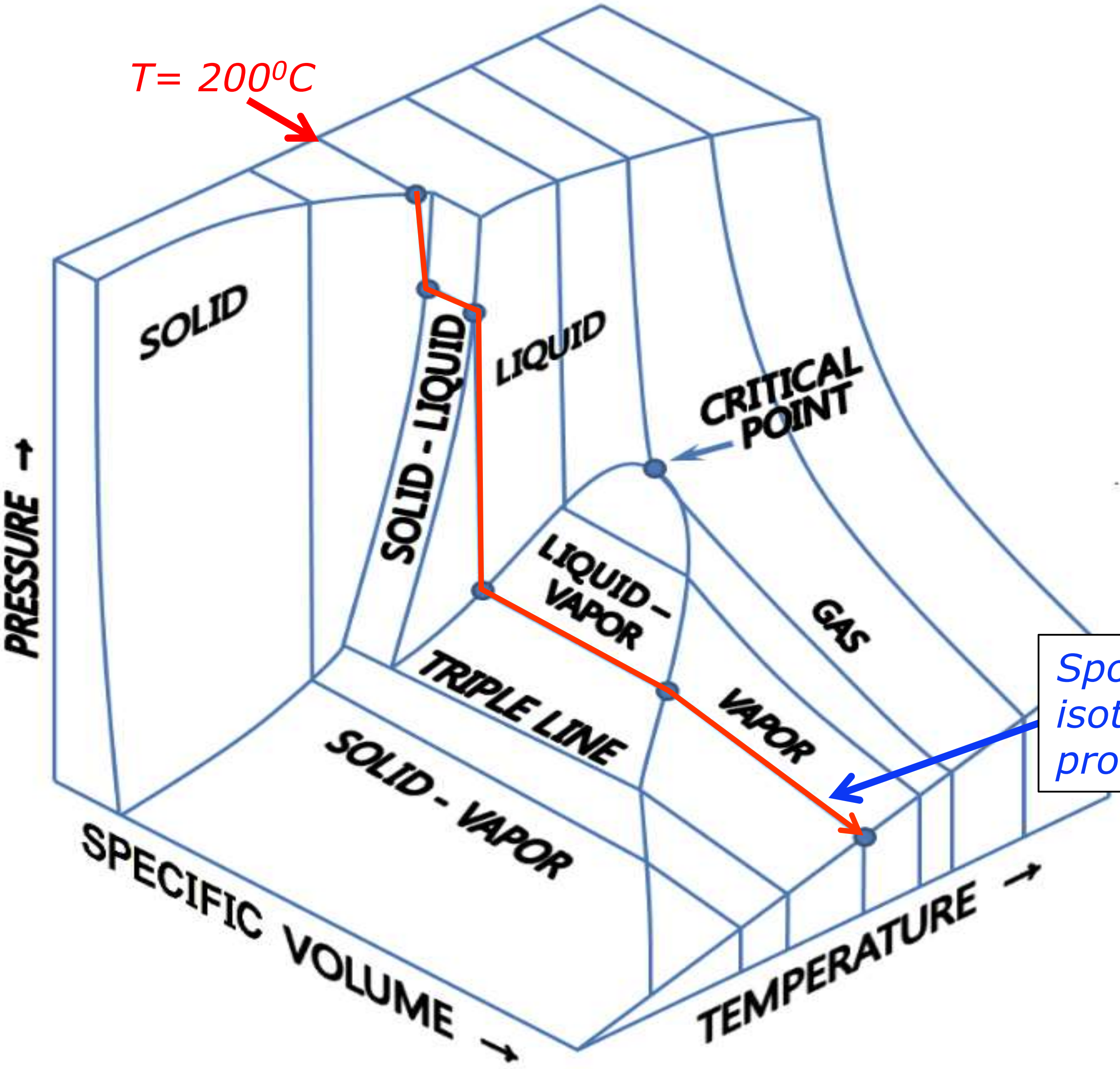
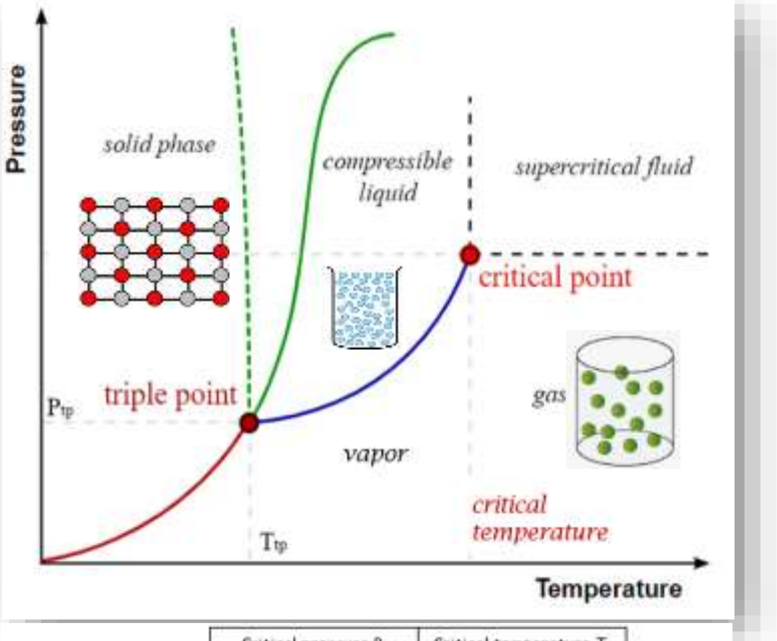
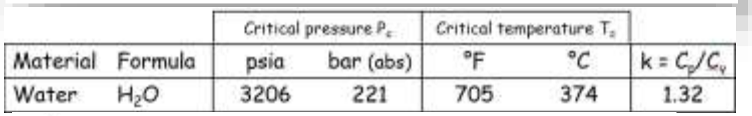
3D Phase Diagram for Water



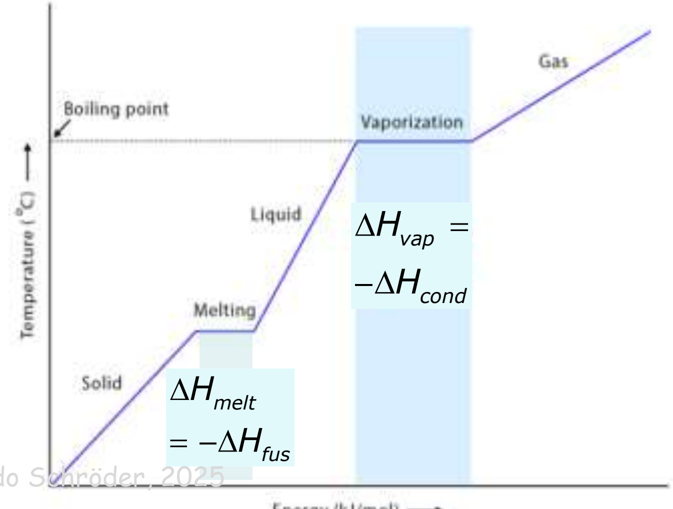
Spontaneous isothermal process

Thermodynamic Energies in Phase Changes





		Critical pressure P_c		Critical temperature T_c		
Material	Formula	psia	bar (abs)	°F	°C	$k = C_p/C_v$
Water	H_2O	3206	221	705	374	1.32



$\Delta H_{vap} = -\Delta H_{cond}$

$\Delta H_{melt} = -\Delta H_{fus}$

Internal structural energy : 1*mole substance*

extensive (additive) state function energy U

Enthalpy = *Structural Energy* +

+ $p - V$ *work to access space*

$\rightarrow \quad \boxed{H = U + P \cdot V}$

Ex. process @ $p = const \rightarrow \Delta H\big|_p = \Delta U + p \cdot dV$

= *extensive state function*

Reference energy H^0 @ *standard state*

$T = 25^0 C,\ P = 1 bar \leftarrow$ *large databases*

$H^0 = 0$ *for pure elemental substances*

Phase changes $\Delta H \neq 0$

$\rightarrow$ *latent heat transfer* $\Delta T = 0$

@ $1\,bar,\ T = 100^0 C$ $\quad (\neq$ *the standard state*)

$H_2O(\ell) \rightarrow H_2O(g) \rightarrow \Delta H_{vap} = +40.7\,kJ/mol$

$H_2O(g) \rightarrow H_2O(\ell) \rightarrow \Delta H_{cond} = -40.7\,kJ/mol$