Thermodynamics Properties

- **Property**
  - any characteristic of a system which can be *quantitatively evaluated* and which is *related to energy* of system
  - examples: *m, V, E, p, T, S, H, ...*
- **Independent Properties**
  - Question: How many *intensive* properties does to take to define a unique *state* for a *known* substance?
  - Answer: **Two -** for simple compressible substances
    - useful work done only by compression/expansion; no E&M fields, no liquid surface tension,...
- So if you know two properties, can predict the rest

State Equations

- Relate TD properties
  - e.g., $Y=Y(T,p)$
- **Examples**
  - Gibbs equation (from 1st and 2nd Laws)

$$\boxed{ds = \frac{de}{T} + \frac{p}{T}dv} \quad \textbf{(II.5)}$$

  - caloric equations of state

$$h = h(T,\rho)$$
$$e = e(T,\rho)$$

- **Simplify by restricting ourselves to perfect gases**
  - obey **Perfect Gas** relation

$$\boxed{\begin{array}{c} p = \rho RT \\ or \\ pv = RT \end{array}} \quad \textbf{(II.6)}$$

Perfect (Ideal) Gases

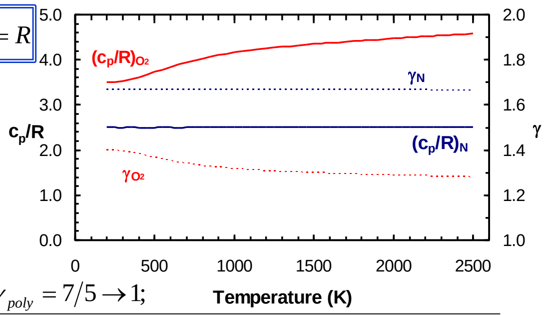
- Thermal (virial) state equation

$$p=\rho RT=\rho\frac{\overline{R}}{\overline{M}}T;\ \overline{R}=8.3143J/mol\cdot K=8.3143kJ/kmol\cdot K$$
$$=1.9858cal/mol\cdot K=1545.3\ ft\cdot lb_f/lbmol\cdot R$$

- "Energy" state equations (**Specific Heats**)

(II.7)
$$\boxed{\begin{aligned}&c_v\equiv\frac{de}{dT};\ c_p\equiv\frac{dh}{dT};\ c_p-c_v=R\\ &\gamma\equiv\frac{c_p}{c_v}=\frac{c_p}{c_p-R}=\frac{1}{1-R/c_p}\\ &\Rightarrow\frac{c_p}{R}\left(=\frac{\bar{c}_p}{\overline{R}}\right)=\frac{\gamma}{\gamma-1}\end{aligned}}$$

bar means per mole



$$\gamma_{atom}=5/3;\gamma_{diatom}=7/5\rightarrow 9/7;\gamma_{poly}=7/5\rightarrow 1;$$

Perfect Gas – Entropic State Eq'n.

- Gibbs Eq. $Tds=de+pdv$

$$\begin{aligned}&=de+\underbrace{pdv+(vdp}-vdp)\\ &=de+\quad d(pv)\quad -vdp\\ &=dh-vdp\end{aligned}$$

$$ds=\frac{dh}{T}-\frac{v}{T}dp$$
$$=\frac{c_p(T)dT}{T}-\frac{R}{p}dp$$

for a P.G.
$dh=c_p dT$
$pv=RT$

From state 1 to state 2 **(II.8)**

$$\int_{s_1}^{s_2}ds=\boxed{s_2-s_1}=\int_{T_1}^{T_2}\frac{c_p(T)dT}{T}-R\int_{p_1}^{p_2}\frac{dp}{p}=\boxed{\int_{T_1}^{T_2}\frac{c_p(T)dT}{T}-R\ln\frac{p_2}{p_1}}$$

$$s_2-s_1=\underbrace{[\phi(T_2)-\phi(T_1)]}_{\text{fn of T only}}-\underbrace{R\ln(p_2/p_1)}_{\text{fn of p only}}$$

p-T-s State Equation

$$s_2 - s_1 = \Delta s_{12} = \left[\Delta\phi_{12}\right] - R\ln\left(p_2/p_1\right) = \int_{T_1}^{T_2} \frac{c_p(T)dT}{T} - R\ln\left(p_2/p_1\right)$$

Cal. Perf. $\boxed{\Delta s_{12} = c_p \ln\left(T_2/T_1\right) - R\ln\left(p_2/p_1\right)}$ **(II.9)**

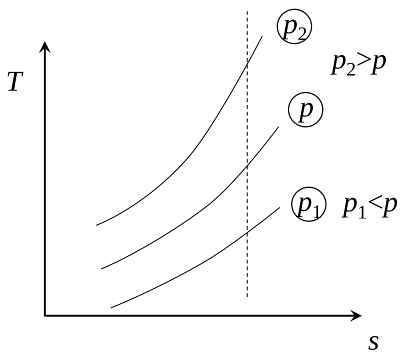
	General	*Calorically Perfect*
• **Pressure ratio**	$\frac{p_2}{p_1} = e^{(\Delta\phi_{12} - \Delta s_{12})/R}$	$\frac{p_2}{p_1} = \left(\frac{T_2}{T_1}\right)^{c_p/R} e^{-\Delta s_{12}/R}$
– **if isentropic** ($\Delta s_{12}=0$)	$\frac{p_2}{p_1} = e^{\Delta\phi_{12}/R}$	$\boxed{\frac{p_2}{p_1} = \left(\frac{T_2}{T_1}\right)^{c_p/R}}$ $= \frac{\gamma}{\gamma-1}$

(II.10)

must be absolute p,T

State Diagrams

- Useful to be able to visualize/graph state relationships
  - in engine (cycle) analysis, *T-s* an important diagram



$$Tds = c_p dT - vdp$$

$$dT = \left(T/c_p\right)ds + \left(v/c_p\right)dp$$

$$= \left.\frac{\partial T}{\partial s}\right|_p ds + \left.\frac{\partial T}{\partial p}\right|_s dp$$

>0 ↑ w/ T↑ | >0

s↑ for T↑ @constant p — p

T↑ for p↑ @constant s — s