Lecture 3

Applications of the 1st and 2nd laws

Main message:

$$TdS = dU + pdV \qquad dU = TdS - p\,dV$$
$$= TdS + \sum_i J_i dX_i$$

- main equation in thermodynamics that we need to remember. By manipulating this, can get any thermodynamic identity that we want.

1) Dependence of U on V – relate to equation of state $p = p(T,V)$

$$TdS = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\left(\frac{\partial U}{\partial V}\right)_T + p\right) dV$$

$$dS = \underbrace{\frac{1}{T} C_V}_{\left(\frac{\partial S}{\partial T}\right)_V} dT + \underbrace{\frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_T + p\right)}_{\left(\frac{\partial S}{\partial V}\right)_T} dV$$

$S = S(T,V)$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \Rightarrow \frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_T + p\right) \Rightarrow \frac{\partial^2 S}{\partial T \partial V} = -\frac{1}{T^2}\left(\left(\frac{\partial U}{\partial V}\right)_T + p\right)$$
$$+ \frac{1}{T}\left(\frac{\partial^2 U}{\partial T \partial V} + \left(\frac{\partial p}{\partial T}\right)_V\right)$$

$$\Rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p}$$

Example: Ideal gas $p = \frac{NkT}{V} \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$

so this is only consistency check

(Actually used Joule's free expansion experiment $\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$
— to identify thermodynamic & ideal gas temperature!)

(entalpy)

1') Similarly, dependence of H on p

$H = U + pV$

$S = S(T, p)$

$H = H(T, p)$

$TdS = dU + pdV = dH - Vdp$

identical manipulations

$$\Rightarrow \boxed{\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V}$$; For ideal gas, $\left(\frac{\partial H}{\partial p}\right)_T = \emptyset$ $\left(\begin{matrix} H = U(T) \\ + NkT \end{matrix}\right)$

$$TdS = \left(\frac{\partial H}{\partial T}\right)_p dT + \left[\left(\frac{\partial H}{\partial p}\right)_T - V\right] dp =$$

$$= \boxed{c_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp}$$

Summary:

1) and 1')

$$\boxed{\begin{aligned} TdS &= c_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV \\ TdS &= c_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp \end{aligned}}$$

– will use in the discussion of response properties

Slightly different derivation of $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$:

$F = U - TS$

$dF = -SdT - pdV \Rightarrow -S = \left(\frac{\partial F}{\partial T}\right)_V$

$-p = \left(\frac{\partial F}{\partial V}\right)_T$

"Maxwell relation" $\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V}$

Mere generally $dF = -SdT + \sum_i J_i dX_i$

$$\boxed{\left(\frac{\partial S}{\partial X_i}\right)_{T, X_{j \neq i}} = -\left(\frac{\partial J_i}{\partial T}\right)_{X_j}}$$

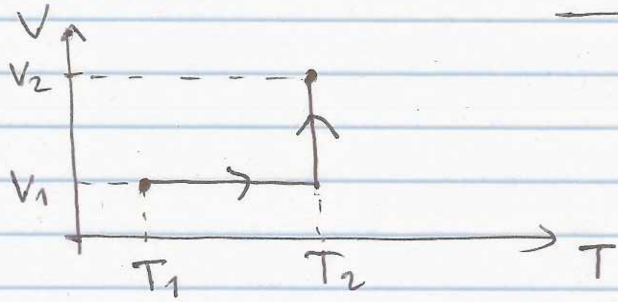
scales, so this is only consistency check).

2) Experimental determination of U, S from equation of state and c_V

Energy $\quad U = U(V,T)$

$$\boxed{dU = c_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV = c_V\, dT + \left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right) dV}$$

Example



$$U_2 - U_1 = \int_{V_1,T_1}^{V_1,T_2} c_V(V_1,T)\, dT + \int_{V_1,T_2}^{V_2,T_2} \left(T_2\left(\frac{\partial p}{\partial T}\right)_V - p\right)\Bigg|_{(V,T_2)} dV$$

Entropy $\quad S = S(V,T)$

$$T\,dS = dU + p\,dV = c_V\, dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

$$\boxed{dS = \frac{c_V}{T}\, dT + \left(\frac{\partial p}{\partial T}\right)_V dV}$$

$$S_2 - S_1 = \int_{V_1,T_1}^{V_1,T_2} \frac{c_V(V_1,T)}{T}\, dT + \int_{V_1,T_2}^{V_2,T_2} \left(\frac{\partial p}{\partial T}\right)_V (V,T_2)\, dV$$

$\Rightarrow$ all thermodynamics can be determined from c_V and equation of state

Example: Ideal gas: $\quad C_V = \frac{3}{2} Nk, \quad pV = NkT$

$$U_2 - U_1 = \frac{3}{2} Nk (T_2 - T_1) \Rightarrow U(V,T,N) = \frac{3}{2} NkT + \text{const}$$

$$S(V_2,T_2) - S(V_1,T_1) = \frac{3}{2} Nk \ln\frac{T_2}{T_1} + Nk \ln\left(\frac{V_2}{V_1}\right) \Rightarrow S(V,T,N) = Nk\left[\frac{3}{2}\ln T + \ln V + \text{const}\right]$$

For U & S to be extensive, we must have $\quad \text{const} = \nu N$, $\text{const}' = \sigma - \ln N$

(to have $\ln \frac{V}{N} = \ln \frac{1}{\rho}$ – intensive quantity)

stat mech $\Rightarrow \nu = 0$, $\quad \sigma = \frac{3}{2} \ln \frac{2\pi m k}{h^2} + \frac{5}{2}$

3) Dependence of C_V on V

$$dS = \underbrace{\frac{C_V}{T}}_{\left(\frac{\partial S}{\partial T}\right)_V} dT + \underbrace{\left(\frac{\partial p}{\partial T}\right)_V}_{\left(\frac{\partial S}{\partial V}\right)_T} dV$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\boxed{\left(\frac{\partial C_V}{\partial V}\right)_T = T \frac{\partial^2 S}{\partial V \partial T} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V}$$

$$C_V(V,T) - C_V(V_0,T) = T \int_{V_0,T}^{V,T} \left(\frac{\partial^2 p}{\partial T^2}\right)_V (V',T)\, dV'$$

$\Rightarrow$ can calculate $C_V(V,T)$ from $C_V(V_0,T)$ and equation of state

> All thermodynamics can be determined from $C_V(V_0,T)$ and equation of state

Example: ideal gas $\quad C_V = \frac{3}{2} N k_B$ – indep. of volume

– consistent with equation of state $\Rightarrow \frac{\partial^2 p}{\partial T^2} = \emptyset$.

If this were not true, we could construct an engine that would violate the second law!

Response functions

$$c_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \quad ; \quad \delta Q = dU + p\,dV \overset{dp=0}{=} \left(\frac{\partial U}{\partial T}\right)_p dT + p\left(\frac{\partial V}{\partial T}\right)_p$$

$$c_p \equiv \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

determined entirely from equation of state $V = V(p;T)$

$$\alpha_p \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$ – thermal expansion coefficient at constant p

$$\varkappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$ – isothermal compressibility

$$\varkappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$ – adiabatic compressibility

Only 3 of the response functions are independent

Lemma: For any variables x, y, z constrained by $f(x,y,z)=0$

$x(y,z)$; $y(x,z)$; $z(x,y)$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$ reciprocity theorem

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

mathematical result that allows faster manipulations of therm. quantities (no physical content)

Proof $x = x(y,z)$ $\quad dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$

$$dy = \underbrace{\frac{1}{\left(\frac{\partial x}{\partial y}\right)_z}}_{\left(\frac{\partial y}{\partial x}\right)_z} dx \underbrace{- \frac{\left(\frac{\partial x}{\partial z}\right)_y}{\left(\frac{\partial x}{\partial y}\right)_z}}_{\left(\frac{\partial y}{\partial z}\right)_x} dz$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y = -\frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$ ▲

! not a chain differentiation!

$$* \quad \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1 \quad \Rightarrow \quad \boxed{\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha_p}{\varkappa_T}}$$

$$* \quad T\,dS = c_V\,dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

$$dS = 0 \quad \Rightarrow \quad c_V = -T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S$$

$$* \quad T\,dS = c_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$dS = 0 \quad \Rightarrow \quad c_p = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_S$$

$$\frac{c_p}{c_V} = \frac{\left(\frac{\partial V}{\partial T}\right)_p}{-\left(\frac{\partial p}{\partial T}\right)_V} \cdot \frac{\left(\frac{\partial p}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial T}\right)_S} = \frac{(\partial V/\partial p)_T}{(\partial V/\partial p)_S} = \frac{\varkappa_T}{\varkappa_S}$$

$$\frac{\left(\frac{\partial V}{\partial T}\right)_p}{-\left(\frac{\partial p}{\partial T}\right)_V} = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} = \left(\frac{\partial V}{\partial p}\right)_T$$

$$\frac{\left(\frac{\partial p}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial T}\right)_S} = \left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial p}{\partial V}\right)_S$$

$p = p(T,S) \quad T = T(V,S)$

$p = p(V,S) = p(T(V,S), S)$

here chain rule (same variable S is kept fixed)

$$* \quad (c_p - c_V)\,dT - T\left(\frac{\partial p}{\partial T}\right)_V dV - T\left(\frac{\partial V}{\partial T}\right)_p dp = 0$$

$$dT = \left(\frac{\partial T}{\partial V}\right)_p dV + \left(\frac{\partial T}{\partial p}\right)_V dp$$

$$\Rightarrow \quad (c_p - c_V)\left(\frac{\partial T}{\partial V}\right)_p = T\left(\frac{\partial p}{\partial T}\right)_V = T\,\frac{\alpha_p}{\varkappa_T}$$

$$(c_p - c_V)\left(\frac{\partial T}{\partial p}\right)_V = T\left(\frac{\partial V}{\partial T}\right)_p$$

– not an indep. equation since $\left(\frac{\partial T}{\partial p}\right)_V = \left(\left(\frac{\partial p}{\partial T}\right)_V\right)^{-1}$ etc

$$\boxed{(c_p - c_V) = T\,\frac{\alpha_p}{\varkappa_T}\left(\frac{\partial V}{\partial T}\right)_p = T\,V\,\frac{\alpha_p^2}{\varkappa_T}}$$

– function of equation of state

α_p & $\varkappa_T$ – obtained from equation of state

$$TdS = \delta Q = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \underbrace{\left(\left(\frac{\partial U}{\partial V}\right)_T + p\right)}_{T\left(\frac{\partial p}{\partial T}\right)_V} dV$$

Response functions:

Specific heats

$$\boxed{\begin{aligned} C_V &\equiv T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \\ C_p &\equiv T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \end{aligned}}$$

– at const. V

– at const. p

Thermal expansion coeff. at constant p

$$\boxed{\alpha_p \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p}$$

Compressibilities:

$$\boxed{\begin{aligned} \varkappa_T &\equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \\ \varkappa_S &\equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \end{aligned}}$$

– isothermal compressibility

– adiabatic compressibility.

Theorem:
Of the 5 response fnctns $C_V, C_p, \alpha_p, \varkappa_T, \varkappa_S$, only 3 are independent (e.g. $C_V, \alpha_p, \varkappa_T$):

$$\circledast \quad C_p = \left(\frac{\partial U}{\partial T}\right)_V + T\left(\frac{\partial p}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V \cdot \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{V\cdot\alpha_p}$$

Use $\left(\frac{\partial p}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_p \cdot \left(\frac{\partial V}{\partial p}\right)_T = -1$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = -\frac{1}{\left(\frac{\partial T}{\partial V}\right)_p \cdot \left(\frac{\partial V}{\partial p}\right)_T} = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha_p}{\varkappa_T}$$

$$\Rightarrow \boxed{C_p = C_V + T \cdot V \cdot \frac{\alpha_p^2}{\varkappa_T}}$$

$$\circledast \quad \frac{C_p}{C_V} = \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V}$$

Use $\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_S \left(\frac{\partial p}{\partial S}\right)_T = -1$

$$\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T = -1$$

$$\frac{C_p}{C_V} = \frac{\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T}{\left(\frac{\partial T}{\partial p}\right)_S \left(\frac{\partial p}{\partial S}\right)_T} = \frac{\left(\frac{\partial V}{\partial S}\right)_T \cdot \left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial T}{\partial p}\right)_S} = \frac{\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial p}\right)_S}$$

Here chain rule, e.g.

$$\left(\frac{\partial V}{\partial S}\right)_T \cdot \left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T$$ since T is kept fixed

$$V(p,T) = V(S(p,T),T)$$

$$\boxed{\frac{C_p}{C_V} = \frac{\varkappa_T}{\varkappa_S}}$$

<u>Application (example)</u> : ideal gas $\quad pV = Nk_BT$

$$V = \frac{Nk_BT}{p}$$

$$\varkappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{p}$$

Invert: for isothermal process, $-\frac{dV}{V\cdot dp} = \frac{1}{p}$, $\frac{dV}{V} + \frac{dp}{p} = 0$

$$d(\ln V + \ln p) = 0 \Rightarrow \boxed{V\cdot p = \text{const}} \text{ — isotherm}$$

Adiabatic process

assume $\frac{c_p}{c_v} = \gamma = \text{const}$

$$\varkappa_S = \frac{\varkappa_T}{\gamma} = \frac{1}{\gamma} \cdot \frac{1}{p}$$

$$-\frac{1}{V}\frac{dV}{dp} = \frac{1}{\gamma}\cdot\frac{1}{p}, \qquad \gamma \frac{dV}{V} + \frac{dp}{p} = 0, \qquad \boxed{pV^{\gamma} = \text{const}}$$

adiabat

Appearance of $\gamma = \frac{c_p}{c_v}$ is more "fundamental" than coincidence, since for any substance

$$\boxed{\frac{\varkappa_T}{\varkappa_S} = \gamma = \frac{c_p}{c_v}}$$

Remark: $\alpha_p, \varkappa_T$ are determined entirely by the equation of state $V = V(p,T)$. Conversely, if we know $\alpha_p, \varkappa_T$, we can recover the equation of state.
Since c_v & equation of state $\Rightarrow$ full thermodynamics, it is not surprising that we can express $c_p, \varkappa_S$ in terms of $c_v, \alpha_p, \varkappa_T$. The above treatment provides concise such expressions.