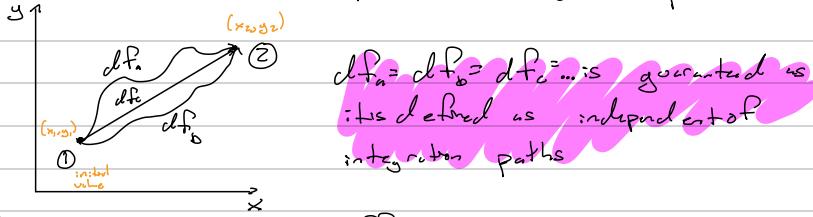




Math Review

① **Differentials** \equiv an infinitesimal change in a function or variable
 ex: If $f = f(x, y)$, then the total differential of f is $df = P(x, y)dx + Q(x, y)dy$
 and is exact and independent of integration paths



② **Partial Derivatives** \equiv the differential change in one variable with respect to a differential change in another variable, while holding other variables fixed/constant

ex: Let $f(x, y) = x^2y + xy + \sin x \sin y$.

$$\begin{aligned} \text{Diff. change in } f & \text{ (} \frac{\partial f}{\partial x} \text{)} @ \text{constant } y = \left(\frac{\partial f}{\partial x} \right) \\ \text{Diff. change in } x & \text{ (} \frac{\partial x}{\partial x} \text{)} \end{aligned}$$

then $\left(\frac{\partial f}{\partial x} \right) = 2xy + \sin y + \cos x \sin y \leftarrow P$

Similarly $\left(\frac{\partial f}{\partial y} \right) = x^2 + x \cos y + \sin x \cos y \leftarrow Q$

Now note that for our total differential, $df = P(x, y)dx + Q(x, y)dy$
 \rightarrow if y is held constant and hence $dy = 0$, $df = P(x, y)dx \Rightarrow \left(\frac{\partial f}{\partial x} \right)_y = P(x, y)$
 \rightarrow similarly for constant x , then $\left(\frac{\partial f}{\partial y} \right)_x = Q(x, y)$

③ **Integration** \equiv continuous sum over differential changes

$$\int f(x) dx$$

Integral \uparrow Differential

1. **Indefinite Integral:** No upper/lower bounds

$$\text{ex: } \int (A + BT + CT^2 + \frac{D}{T} + \frac{E}{T^2}) dT \quad \text{where } A, B, C, D, E \text{ are constants, } T \text{ is temperature}$$

$$= AT + \frac{1}{2}BT^2 + \frac{1}{3}CT^3 + DT - E + (\text{constant})$$

2. **Definite Integral:** Specified lower & upper bounds (no constant of integration)

$$\int_{T_0}^{T_1} (A + BT) dT = \left[AT + \frac{B}{2}T^2 \right]_{T=T_0}^{T=T_1} = A(T_1 - T_0) + \frac{B}{2}(T_1^2 - T_0^2)$$

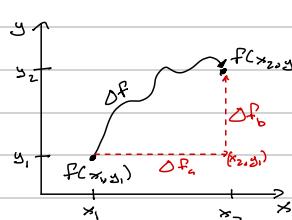
Summary - Common points of confusion!

① **Differential:** infinitesimal changes denoted df

② **Derivative:** change in one variable with respect to another (\approx differential / another differential)
 ex: $\frac{df}{dx}, \frac{df}{dt}, \frac{df}{dx}_y$

③ **Integral:** Continuous sum over differential changes
 ex: $f = f(x)$: $f(x_b) - f(x_a) = \int_{x_a}^{x_b} df$ problem: Need to integrate w.r.t. variable in our bounds of integration $= \int_{x_a}^{x_b} \left(\frac{df}{dx} \right) dx$ derivative!

ex: $f = f(x, y)$:



$$f(x_2, y_2) - f(x_1, y_1) = \Delta f = \Delta f_a + \Delta f_b$$

$$= \int_{x_1}^{x_2} \left(\frac{\partial f}{\partial x} \right)_{y=y_1} dx + \int_{y_1}^{y_2} \left(\frac{\partial f}{\partial y} \right)_{x=x_2} dy$$

We can do this bc the differential is independent of path

* Math no-no!

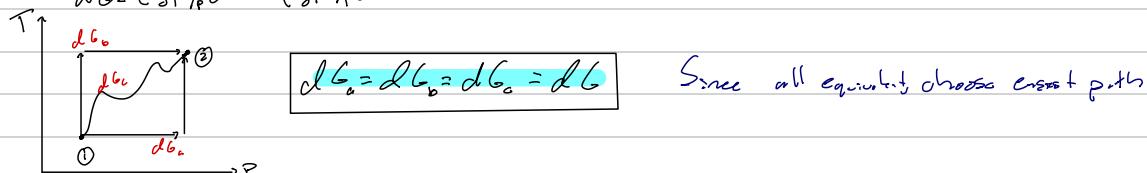
$\times \Rightarrow \int \frac{df}{dx}$ cannot be evaluated! Missing the differential!

\hookrightarrow Must integrate over differential changes

$\checkmark \Rightarrow \int \left(\frac{df}{dx} \right) dx$ is allowed!

Chapter 1 - Thermodynamic Properties

Thermodynamic Properties are state functions that do not depend on path and have exact differentials.
 ex: $G = G(T, P)$ Gibbs Free Energy
 $dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$



Inexact Differentials are path functions (i.e., they do depend on path)

ex: work (w) and heat (Q)

→ dW and dQ do depend on path

→ use notation δQ and δW to denote an inexact differential

What is Thermodynamics?

↳ A self-contained, logically consistent theory that can be expressed in two laws:

• First Law: Conservation of Energy

$\Delta E_{\text{univ}} = 0$ for any process

• Second Law: Entropy increases

$\Delta S_{\text{univ}} \geq 0$ for any process

• Two benefits of the 2nd Law

(i) Is our process consistent with 2nd Law?

(ii) Entropy of system + surroundings should reach a maximum over time.

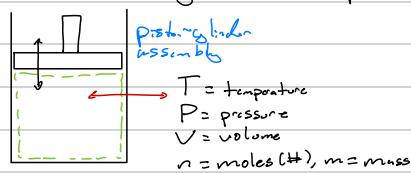
① System and Surroundings



• Three Types of Systems

	"closed"	"open"	"isolated"
energy transfer	yes	yes	No
mass transfer	No	yes	No

② Thermodynamic Properties of Fluids (mostly gases & liquids, only some solids)



Types of Properties

- (i) extensive = varies w/ size of system
- (ii) intensive = independent of system size

Q: Which of the following thermodynamic properties are intensive? (out of P, T, n, V, ρ)

$$\textcircled{1} P, T, n$$

$$\textcircled{3} V, n$$

$\textcircled{2} P, T, \rho$ None of these depend on how large the system is, or how much stuff is in it!

P	V	T	n
↑ intensive (C_{∞})	↑ extensive (C_{ext})	↑ int	↑ ext

density

We can convert ext quantities to int ones:

extensive = "specific property" ↪ lowercase with no $\frac{1}{m}$
 mass → intensive quantity normalized by mass

$$\text{ext: } \frac{\text{Volume}}{\text{mass}} = \frac{V}{m} = \frac{1}{\rho} \quad \text{specific volume}$$

extensive = "molar property" ↪ lowercase w/ subscript m
 moles → intensive

$$\text{ext: } \frac{\text{Volume}}{\text{moles}} = V_m \quad \begin{array}{l} \text{relation for ext} \\ \text{readily & agreed} \\ \text{is distinct from textbook} \end{array}$$

③ "State" of a System

- The "state" of a system depends on its thermodynamic properties
 ↳ can be described by the Gibbs phase rule:

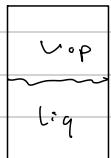
$$f = m - \pi + 2 \quad \text{for non-reactive systems}$$

\uparrow degrees of freedom
 \uparrow # of chemical species
 \uparrow # of phases

o Degrees of Freedom \Rightarrow # of intensive properties that must be specified to constrain properties of system

- To fully specify a state, also need to know amount of material

Example: Vapor-liquid mixture of H_2O



$$m=1 \quad \pi=2 \quad \Rightarrow f=1$$

mol/mol of liq mol/mol vap

$$V_{\text{tot}} = V = V_{m,\text{L}} n_{\text{L}} + V_{m,\text{V}} n_{\text{V}} \quad \Rightarrow \text{divide by } V_{\text{tot}} = n = n_{\text{L}} + n_{\text{V}}$$

$$\Rightarrow \frac{V}{n} = V_m = (1-x) V_{m,\text{L}} + x V_{m,\text{V}}$$

\uparrow average molar volume
 $x \equiv \text{"quality"}$

$$\text{Also: } \beta = (1-x)\beta_{\text{L}} + x\beta_{\text{V}}$$

We can't for example specify V_m for each phase

→ constrains all other intensive properties

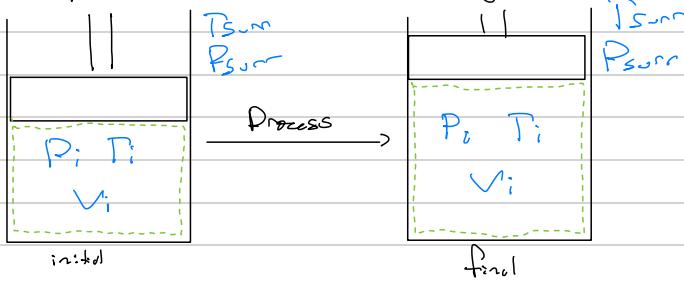
Also need to specify total amount in each phase

$$\rightarrow V_{\text{tot}} = V_{\text{liq}} + V_{\text{vap}}$$

$Q_{\text{liq}} = \text{mole or mass fraction of } \text{H}_2\text{O}$
 for saturated (vapor) mixture

④ Processes

- A process is a change in the system



4 Special Types of Processes

- Isothermal** $\rightarrow \text{const } T$
- Isobaric** $\rightarrow \text{const } P$
- Isochoric** $\rightarrow \text{const } V$
- Adiabatic** $\rightarrow \text{No heat transfer to/from sum}$
↳ can also be described as well-insulated

⑤ Equilibrium

- A system does not change @ equilibrium and there is no driving force for change

→ Examples:

(i) Thermal Equilibrium $\rightarrow T_{\text{sys}} = T_{\text{sum}}$ (also btwn phases)

(ii) Force/mechanical $\rightarrow P_{\text{sys}} = P_{\text{sum}}$

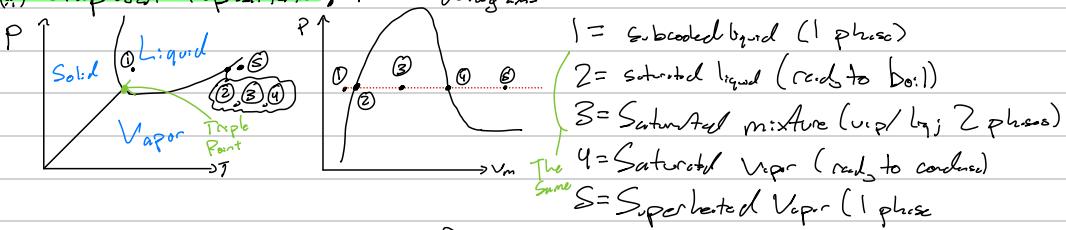
(iii) Phase Equilibrium \rightarrow Composition of phases is constant

(iv) Chemical Equilibrium \rightarrow No mass transfer into/out of a phase, or no net chemical reaction

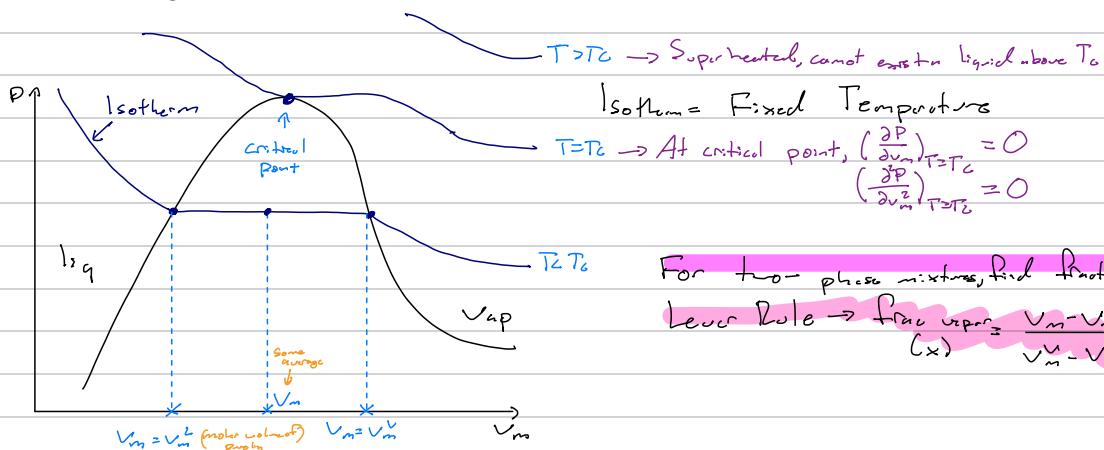
Thermodynamic Property Sources

(i) Experiment $\rightarrow P, T, V, \dots$

(ii) Graphical Representation: PVT diagrams



• PVT diagrams are very useful!



$T = T_c \rightarrow$ Isotherm = Fixed Temperature

$$T = T_c \rightarrow \text{At critical point, } \left(\frac{\partial P}{\partial V_m}\right)_{T=T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial V_m^2}\right)_{T=T_c} = 0$$

For two-phase mixtures, find fraction of vapor using mass balance

$$\text{Lever Rule} \rightarrow \text{frac vapor} = \frac{V_m - V_m^L}{V_m - V_m^V} \quad (x) \quad (\text{Derivation on Canvas})$$

(iii) Thermodynamic Tables (ex. steam tables \rightarrow Appendix B of Kotz et al.)

• Always use steam tables for water

• Linear interpolation required for conditions between values in the table

(iv) Equations of State

\rightarrow ideal gas law, $PV_m = RT$

\rightarrow van der Waals...

(v) Statistical Mechanics (molecular calculations)

\hookrightarrow not focused on in this course

Final Notes about (Potentially) 2-phase systems

- If $V \geq V_{i,c}^{sat}$ you have pure vapor
- If $V_{i,c}^{sat} > V > V_{i,l}^{sat}$ you have a mixed phase
- If $V_{i,l}^{sat} \geq V$ you have pure liquid

Similar ideas work for any specific (or master) property: v_m, u_m, h_m, \dots

Example A rigid 100L container w/ saturated water @ 100°C. If the initial reaches the critical point.

a) Draw the process on a P-v diagram.

initial (i)

$$V_i = 100L$$

$$T_i = 100^\circ C$$

saturated

final (f)

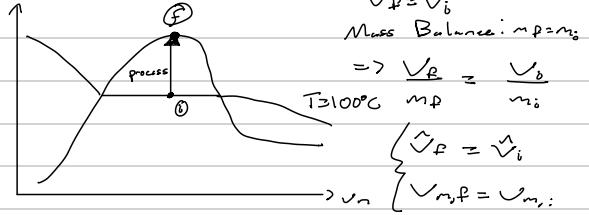
$$V_f = 100L = V_i$$

$$T_f = T_c$$

$$P_f = P_c$$

process

→ critical point



b) Find the mass and initial quality.

(outlines)

→ mass balance: $m_f = m_i$

rigid: $V_f = V_i = V$

$$\rightarrow V_f = V_i = V$$

Steam Tables

because P_c, T_c state is a crit point

$$V_p = V_i = V_c = 0.0033155 \frac{m^3}{kg}$$

$$V = 0.0033155 \frac{m^3}{kg}$$

bottom of tube

↳ of temp → $V_{i,g} = 0$

$$M = \frac{V}{V} = \frac{100 L}{0.0033155 \frac{m^3}{kg}} \times \frac{1 m^3}{1000 L} = 31.6 \text{ kg}$$

(continued)

$$V_i = V_{i,L}^{sat} (1-x) + V_{i,V}^{sat} x$$

$$x = \frac{V_i - V_{i,L}^{sat}}{V_{i,V}^{sat} - V_{i,L}^{sat}} = 0.0015 \quad (\text{nearly all liquid})$$

S + Steam @ 100°C

$$V_{i,L}^{sat} = 0.001047 \frac{m^3}{kg}$$

$$V_{i,V}^{sat} = 1.4194 \frac{m^3}{kg}$$

$$\rightarrow V_{i,L}^{sat} < V < V_{i,V}^{sat} \Rightarrow L/V mix$$

Chapter 2 - The First Law of Thermodynamics

- First Law: $\Delta E_{\text{univ}} = 0$ or $E_{\text{univ}} = \text{constant}$

Q: What is E_{univ} ?

1) Macroscopic Kinetic Energy ($E_k = \frac{1}{2} m (v)^2$)

2) Macroscopic Potential Energy ($E_p = mg$)

3) Internal Energy (U_m): all energy at molecular level
 $\rightarrow U_m$ includes:

- molecular kinetic energy $\rightarrow T$

- molecular potential energy (attractions/repulsions between molecules)

o Changes in U_m come from:

First part of the class - changes in T, P , or other properties

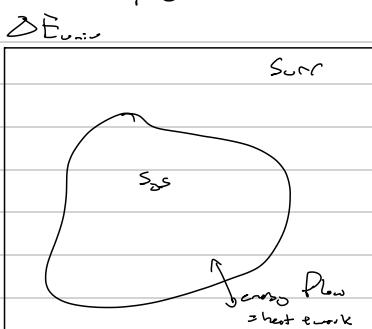
- phase changes

- chemical reactions (breaking/forming chemical bonds)

Note: An ideal gas by definition has no (0) potential energy between molecules

$U_m = U_m(T)$ only true for ideal gases

- We can simplify 1st Law (for closed systems):



$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}} = Q + W$$

heat work

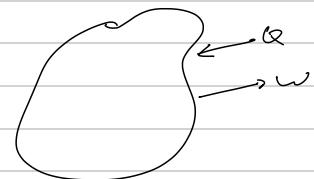
Q: Heat and work are flowing across the system boundary. What can we say about Q and W?

1) both $Q & W > 0$

2) $Q > 0, W < 0$

3) $Q < 0, W > 0$

4) both $Q & W < 0$



Recall $\Delta E = \text{internal} + \text{kinetic} + \text{potential}$

$$\Delta E_{\text{sys}} = \Delta U + \Delta E_k + \Delta E_p$$

Leave off "sys" for convenience

so, exterior: $\Delta U + \Delta E_k + \Delta E_p = Q + W$ First Law for closed systems

interior: $\Delta U + \Delta E_{\text{int}} + \Delta E_{\text{p,int}} = Q + W$

And for small processes, $\Delta u \rightarrow du$

$$du + dE_{\text{int}} + dE_{\text{p,int}} = \delta Q + \delta W \leftarrow Q \text{ and } W \text{ are moment differentials for path functions}$$

Accumulation

How do we calculate variables in the first law?

Not currently focused on
 in this course → ECHE360

① Heat (Q): energy transferred across system boundaries by Temperature gradients (conduction, radiation, etc.)

② Work (W): this class!

a) System boundary moves against an external force

$$\rightarrow \text{From physics, } W = \int_{\text{path}} \vec{F}_E \cdot d\vec{x}$$

where $\vec{F}_E = -P_E \vec{A}$

$$\text{so then, } W = - \int_{\text{path}} P_E \vec{A} \cdot d\vec{x} = - \int P_E dV \quad \text{"PV work"}$$



→ Calculating PV work requires us to know external pressure

* P_E does not always equal P_{ext}

b) Shaft Work (W_s)

example: propeller in fluid (macroscopic, not PV)

$$\therefore W = W_s - \int P_E dV$$



Work (and Heat) can be transferred either reversibly or irreversibly.

Reversible Processes - Characteristics & overview

- a) Slow → never more than differentially away from equilibrium
- b) Driven by small changes in forces (or pressures)
- c) Can be reversed at any point
- d) No friction or dissipation → highly idealized process

New
Rec'd
T_{ip} Brovo
21
7

Ex

Reversible work for ideal gas expansion under isothermal conditions.



- isothermal → T is constant
- ideal gas → $PV_m = RT$
- work → PV work → $W = - \int P_E dV$
- mole balance → $n = \text{constant}$ (closed sys)

• reversible → $P_E \approx P$

$$\text{Thus, } W = - \int P_E dV \stackrel{\text{rev.}}{\approx} - \int P dV \\ \stackrel{\text{IGL}}{=} - \int \frac{RT}{V_m} d(V_{m,f} - V_{m,i})$$

n is constant

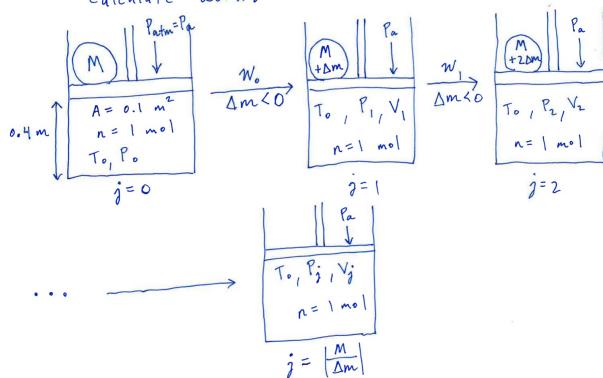
$$\frac{W}{n} = w_m = - RT_i \int_{V_{m,i}}^{V_{m,f}} \frac{dV_m}{V_m}$$

$$w_m = - RT_i \ln \left(\frac{V_{m,f}}{V_{m,i}} \right)$$

reversible work,
isothermal,
ideal gas

ex: ideal gas in a piston expands isothermally in increments of changes in external pressure.

calculate work.



• mole balance: $n = \text{const} = 1 \text{ mol}$

• final mass = 0

• ideal gas: $nRT_0 = P_0V_0 = P_1V_1 = P_2V_2 = \dots = P_jV_j$

• isothermal: $T = \text{const} = T_0$

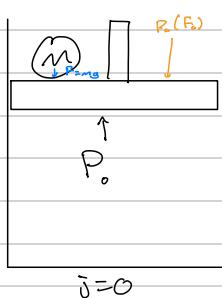
• PV work def'n → $W = - \int P_E dV$ external pressure

↳ what is P_E ?

• At eq. P_E should equal P_{ext}

• pressure / force balance:

Pressure / Force Balance



$$\text{initial } (j=0): A P_0 = A P_{E,0} \Rightarrow A \left(\frac{Mg}{A} + P_0 \right)$$

$$\rightarrow P_0 = P_{E,0} + \frac{Mg}{A}$$

$$\text{Similarly } (j=1): P_1 = P_{E,1} = \left(\frac{(M+\Delta m)g}{A} + P_0 \right)$$

$$W_0 = - \int_{V_0}^{V_1} P_{E,0} dV = - P_{E,0} \int_{V_0}^{V_1} dV = - P_{E,0} (V_1 - V_0) = - P_{E,0} \left(\frac{P_0 V_0}{P_1} - V_0 \right) = - V_0 (P_0 - P_1)$$

cross-sections
area of piston
rock
 $\Delta m < 0$ for this problem given

$$\text{Sub. ideal g. law} \\ P_1 V_1 = P_0 V_0$$

$$\text{Now, sub } P's \text{ from force balance} = - V_0 \left[\left(P_0 + \frac{Mg}{A} \right) - \left(P_0 + \frac{Mg + \Delta m g}{A} \right) \right] = + V_0 \cdot \frac{\Delta m g}{A} < 0$$

negative indicates S₂ &
class work

$$\text{Similarly, } W_1 = - P_{E,2} \Delta V = - P_2 (V_2 - V_1) = - P_2 V_2 \left(1 - \frac{V_1}{V_2} \right) = - P_0 V_0 \left(1 - \frac{V_1}{V_2} \right) = - P_0 V_0 \left(1 - \frac{P_2}{P_1} \right)$$

$\frac{V_1}{V_2} < 1$
 $P_2 < P_1$

$$\rightarrow \text{use force balance} = - V_0 \left(P_0 + \frac{Mg}{A} \right) \left(\frac{\left(- \frac{\Delta m g}{A} \right)}{P_0 + \frac{Mg}{A} + \frac{\Delta m g}{A}} \right)$$

$$\downarrow P_1$$

$$\Rightarrow W_1 = \frac{V_0 \Delta m g}{A} \cdot \frac{P_0 + \frac{Mg}{A}}{P_0 + \frac{Mg}{A} + \frac{\Delta m g}{A}} < 0$$

Expansion → S₂ & class work

Example Continued

$$W_2 = -P_3(V_3 - V_2) = \frac{V_0 \Delta mg}{A} \frac{\frac{mg}{A}}{P_a + \frac{mg}{A} + \frac{\Delta mg}{A}} \text{ etc...}$$

(from $j=2$
to $j=3$)

so, total work done is:

$$W_{\text{tot}} = \sum_{j=0}^{j=1 \text{ to } j-1} W_j = \sum_{j=0}^{j=1 \text{ to } j-1} \left[\frac{V_0 \Delta mg}{A} \cdot \frac{\frac{mg}{A}}{P_a + \frac{mg}{A} + j \frac{\Delta mg}{A}} \right]$$

What happens w/ different $\Delta m's$? Suppose $M = 1020 \text{ kg}$

Final State	$\Delta m (\text{kg})$	$W_{\text{tot}} (\text{J})$
$j=1$	-1020	-4000
$j=2$	-510	-4666
$j=3$	-340	-4928
:	:	:

Thermodynamic properties (i.e., path independent quantities) like T, P, V do not change between initial and final states between scenarios.

→ But work is not a thermodynamic property.
It is path dependent

As we increase the number of steps w/ smaller changes per step, magnitude of work done by the system on the surroundings increases

The Limit? $\lim_{\Delta m \rightarrow 0}$ = reversible process w/ max work done by system on surroundings

($P_E \approx P_{\text{sys}}$ for all steps j)

$$\text{Reversible: } W = - \int_{V_0}^{V_F} P_B dV = - \int_{V_0}^{V_F} P dV$$

$P_B = P$ for a reversible process
changes happening very slowly, so
 $P \approx P_E$ (small changes)

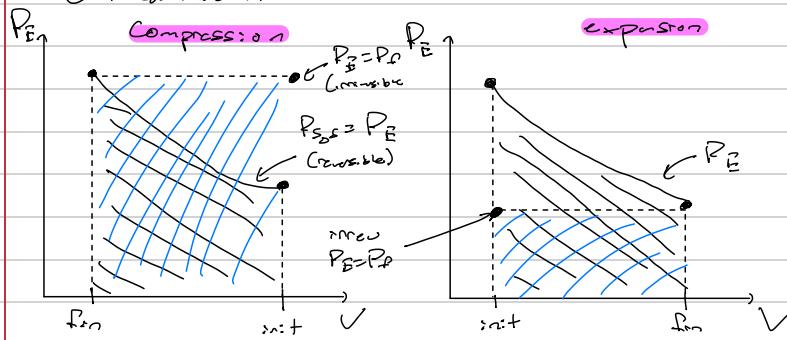
This is a reason why assuming a reversible process can be convenient. $W_{\text{re}} = -5545 \text{ J}$

We've shown that, for closed systems that undergo an isothermal reversible change in Volume, that:

$$W_{\text{isoth}} = -RT \ln \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right)$$

→ If a process were reversible and $V_F < V_i$:

- ① $|W_{\text{min,rev}}| > |W_{\text{max,rev}}|$ This is compression $P_E > P$
- ② $|W_{\text{min,rev}}| < |W_{\text{max,rev}}|$ True for expansion
- ③ $|W_{\text{min,rev}}| = |W_{\text{max,rev}}|$
- ④ Need more information



$$|W_{\text{min,rev}}| > |W_{\text{max,rev}}| \quad |W_{\text{min,rev}}| < |W_{\text{max,rev}}|$$

$$W = - \int P_E dV$$

Internal Energy

• How do we calculate ΔU (dU)?

→ Several Options:

(i) Property tables (NIST, steam tables)

(ii) Specific (molar) heat capacities

a) Ideal Gas: $U_m = U_m(T)$ only (Combination of Temperature)
 $\rightarrow \text{Thus, } C_{v,m} = \frac{dU_m(T)}{dT}$ for ideal gas only

Typically correlations are used: $C_{v,m}(T) = A + BT + CT^2 + \frac{D}{T^2} + ET^3$ where $A-E$ are constants for the gas

Reminder: $C_{v,m} = \left(\frac{\partial U_m}{\partial T} \right)_{V_m} = \frac{dU_m(T)}{dT}$
 \uparrow constant volume
 \uparrow generally true
 \uparrow ideal gas only

Similarly,
 $C_{p,m} = \left(\frac{\partial h_m}{\partial T} \right)_P = \frac{dh_m(T)}{dT}$
 \uparrow constant pressure
 \uparrow generally true
 \uparrow ideal gas only

Enthalpy (h_m)

• Mathematically: $h_m = U_m + PV_m$ (general defn)

→ For ideal gas, $PV_m = RT$

$$\therefore h_m = U_m(T) + RT \Rightarrow h_m = h_m(T) \text{ only for an ideal gas}$$

Note that heat capacities are defined for a single phase.

How to Measure $C_{p,m}$

→ closed system, calorimeter, system @ const P

const P → $P_E = P$ (force balance)

1st Law: $dU_m = dq_m - Pdv_m$ ($P_E = P$)

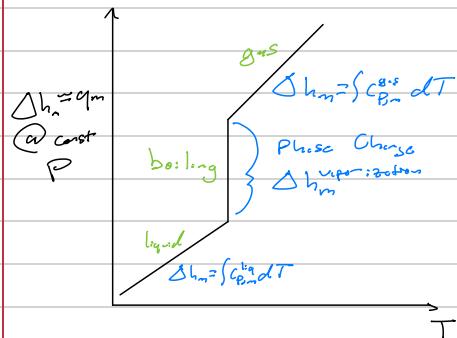
$dU_m = dq_m - d(PV_m)$ can make this more only bc Pressure P is constant

$$dU_m + d(PV_m) = dq_m$$

$$\underbrace{d(U_m + PV_m)}_{h_m} = dH_m = C_{p,m}dT = dq_m \quad \leftarrow \text{measure } q_m \text{ @ const } P$$

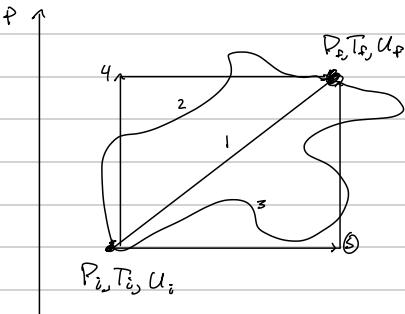
\leftarrow measure T to determine h_m & $C_{p,m}$

③ Latent Heat \equiv enthalpy (or internal energy) of a phase change



Calculation Paths

Used to calculate changes in thermodynamic properties as these do not depend on path ($T, P, V_m, U_m, h_m, \dots$)

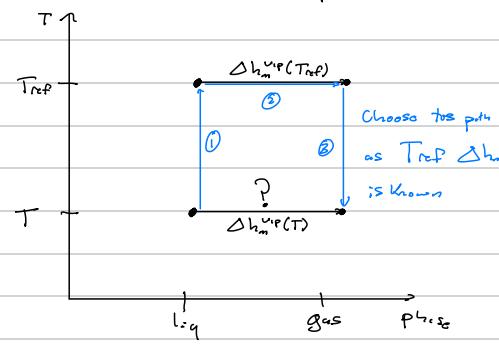


$$\Delta U = U_f - U_i$$

$$= \Delta U_1 = \Delta U_2 = \Delta U_3 = \Delta U_f$$

True for any process!

We can use calculation path to find $\Delta h_m^{vp}(T)$



* T_{ref} is usually 298K

Solution:

$$\Delta h_m^{vp}(T) = \Delta h_m^{vp} + \Delta h_{m2} + \Delta h_{m3}$$

$$\textcircled{1} \text{ Sink phase heating/cooling } \Delta h_{m1} = \int_{T_{ref}}^T C_{P,m}^{lq} dT$$

$$\textcircled{2} \text{ Phase change at } T_{ref}; \Delta h_{m2} = \Delta h_m^{vp}(T_{ref})$$

$$\textcircled{3} \text{ Sink phase cooling/heating } \Delta h_{m3} = \int_{T_{ref}}^T C_{P,m}^{ss}(T) dT$$

$$\therefore \Delta h_m^{vp}(T) = \Delta h_m^{vp}(T_{ref}) + \int_{T_{ref}}^T [C_{P,m}^{ss}(T) - C_{P,m}^{lq}(T)] dT$$

Example 1st Law w/ Property Tables

A rigid container has sat'd water @ 2 bar and quality of $x=0.42$. The water is heated to 540°C. Find the final pressure and the $\Delta \hat{U}, \hat{q}$, and \dot{m} for the process.

initial	final
$\text{Sat'd } H_2O$ $x = 0.42$ $P = 2 \text{ bar}$ V_i	$T_f = 540^\circ\text{C}$ $V_f = V_i (\text{rigid})$

Process:
closed system
constant volume

- initial state is sat'd water, $x = 0.42$
- rigid $\rightarrow V_f = V_i$, and $\dot{V}_f = \dot{V}_i = 0$
- closed system $\rightarrow m_i = m_f$ From mass balance
- water is heated $\rightarrow q \neq 0$
- $\dot{W}_s = 0$ no moving parts or mixing
- $\dot{W} = - \int_{V_i}^{V_f} P_E dV = 0$ (no volume change)
- $\rightarrow KE, PE / mg$ small and negligible

$$1^{\text{st}} \text{ law: } \Delta \hat{U} = \hat{q} + \dot{W}$$

$$\Delta \hat{U}: \text{initial} \rightarrow \text{sat'd water @ } P_{s,t} = 2 \text{ bar (0.2 MPa)}$$

Tab B4: $\hat{u}_i = 504.47 \frac{\text{kJ}}{\text{kg}}$ $\hat{v}_i = 0.001061 \frac{\text{m}^3}{\text{kg}}$ $\hat{C}_i = 1385 \frac{\text{kJ}}{\text{kg}}$ $\hat{C}_i = 0.373 \frac{\text{m}^3}{\text{kg}}$	$\hat{u}_f = 2529.5 \frac{\text{kJ}}{\text{kg}}$ $\hat{v}_f = 0.8857 \frac{\text{m}^3}{\text{kg}}$
---	---

range

$$\hat{v}_f = x \hat{v}_s + (1-x) \hat{v}_l$$

$$\text{Final: Known } T_f = 540^\circ\text{C}, V_f = 0.373 \frac{\text{m}^3}{\text{kg}} \text{ (rigid)}$$

Table B.2 shows $T_f > T_c \rightarrow$ superheated steam

- Interpolate super heated water vapor tables (B4)
- $\rightarrow P_s = 10 \text{ bar (1 MPa)}$

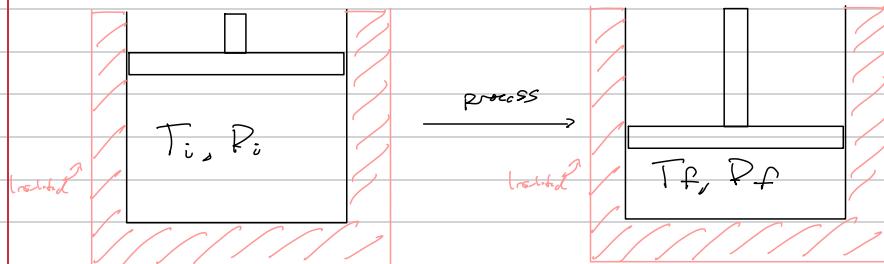
$$\hat{u}_f = 3194 \frac{\text{kJ}}{\text{kg}}$$

$$1^{\text{st}} \text{ law: } \Delta \hat{U} = \hat{q}$$

$$\Delta \hat{U} = \hat{u}_f - \hat{u}_i = 1839 \frac{\text{kJ}}{\text{kg}}$$

$P_f = 10 \text{ bar}$
$\Delta \hat{U} = \hat{q} = 1839 \frac{\text{kJ}}{\text{kg}}$
$\dot{m} = 0$

Example: Reversible adiabatic expansion/compression of an ideal gas with $C_{v,m} = \text{constant}$.
Relate P_i, P_f, V_i, V_f



- closed, mass/mol fixed: $nF = n$
- 1st Law: $dU = \delta Q + \delta W$
- ideal gas $\nabla C_{v,m}dT$
- $P_B dV$ (defn of P_{bulk})
- Reversible $P_B = P$

$$\rightarrow nC_{v,m}dT = -P_B dV$$

$$nC_{v,m}dT = -P dV$$

$$\cancel{n} C_{v,m}dT = -\cancel{\frac{RT}{V}} dV$$

$$\int_{T_0}^{T_f} \frac{C_{v,m}}{T} dT = \int_{V_i}^{V_f} -\frac{R}{V} dV$$

$$\text{If } C_{v,m} = \text{const} \Rightarrow C_{v,m} \ln\left(\frac{T_f}{T_i}\right) = -R \ln\left(\frac{V_f}{V_i}\right)$$

$$\text{take exp: } \left(\frac{T_f}{T_i}\right)^{C_{v,m}} = \left(\frac{V_f}{V_i}\right)^{-R}$$

$$\Rightarrow C_{p,m} = C_{v,m} + R \quad (\text{notes to follow})$$

$$P_f V_f^{\frac{C_{p,m}}{C_{v,m}}} = P_i V_i^{\frac{C_{p,m}}{C_{v,m}}}$$

ideal gas, constant $C_{v,m}$, reversible
and adiabatic

Final Notes on Ideal Gas Heat Capacities

$$\Delta h_m = \int_{h_{m,1}}^{h_{m,2}} dh_m = \int_{T_1}^{T_2} C_{p,m} dT \quad (\text{always true for ideal gas})$$

$$\text{Because } h_m \equiv U_m + PV_m = U_m + RT$$

$$\frac{dh_m}{dT} = \frac{dU_m}{dT} + R$$



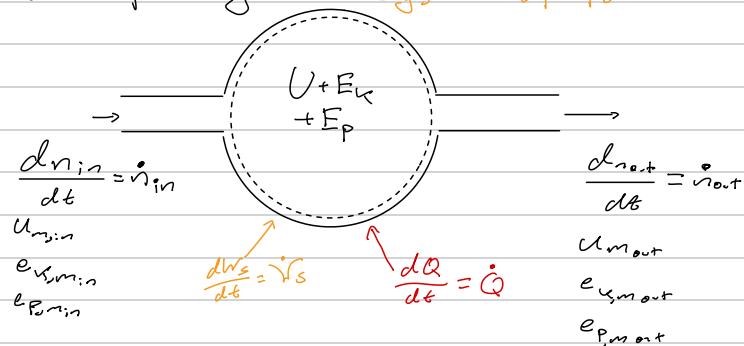
1.G.

$$C_{p,m} = C_{v,m} + R$$

↑ from ∂T
only ↑ from ∂T only

(for ideal gas)

Skip §2.8.2.1 1st Law Open Systems e.g. turbines, pumps, reactors...



* Important Calculus Note:

$$\dot{\nu}_{in} = \frac{d\dot{m}_{in}}{dt} \neq \dot{m}_{in}$$

discrete ↑ differential ↑

Form of PV Work?

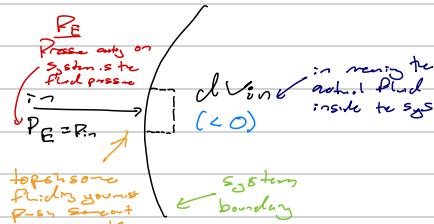
→ Flow Work

Rate of flow work:

$$\frac{dW_{flow}}{dt} = \dot{W}_{flow} = -P_E \frac{dV_{in}}{dt}$$

$$= -P_{in} \frac{d(V_{in} m_{in})}{dt} = -P_{in} \frac{d(m_{in} V_{in})}{dt}$$

$$= -P_{in} \frac{d(m_{in} V_{in})}{dt}$$



$$= P_{in} \frac{d(m_{in} V_{in})}{dt} = P_{in} V_{in} \frac{d\dot{m}_{in}}{dt} = P_{in} V_{in} \dot{\nu}_{in} = \dot{W}_{flow} \because \text{molar rate} = \frac{\text{Rate}}{\dot{\nu}_{in}} = (P_{in} V_{in})_{in}$$

= flow work on sys

→ $P > 0, V_m > 0$, so flow work $\dot{W}_{flow} > 0$ always

⇒ Add flow work to energy balance

$$\frac{d}{dt} (U + E_k + E_p) = \dot{Q} + \dot{W}_s + \dot{\nu}_{in} (U_{in} + e_{kin,in} + e_{pot,in}) + \dot{\nu}_{in} (P_{in} V_{in})_{in}$$

accumulation

$$- \dot{\nu}_{out} (U_{out} + e_{kin,out} + e_{pot,out}) - \dot{\nu}_{out} (P_{out} V_{out})_{out}$$

Result: $h_m \equiv U_m + P_m$

$$\frac{d}{dt} (U + E_k + E_p) = \dot{Q} + \dot{W}_s + \dot{\nu}_{in} (h_m + e_{kin,in} + e_{pot,in}) - \dot{\nu}_{out} (h_m + e_{kin,out} + e_{pot,out})$$

First Law, Open Systems

Can also write on a mass basis:

IF open system is at steady-state

- no mass/moles accumulating in sys
- mass balance, $\frac{d\dot{m}}{dt} = 0 = \dot{\nu}_{in} - \dot{\nu}_{out} \Rightarrow \dot{\nu}_{in} = \dot{\nu}_{out} = \dot{\nu}$

- no change in energy of system

$$\frac{d}{dt} (U + E_k + E_p) = 0$$

- no change in properties with time

IF NOT steady-state

$$\rightarrow \text{mole balance: } \frac{d\dot{m}}{dt} = \dot{\nu}_{in} - \dot{\nu}_{out}$$

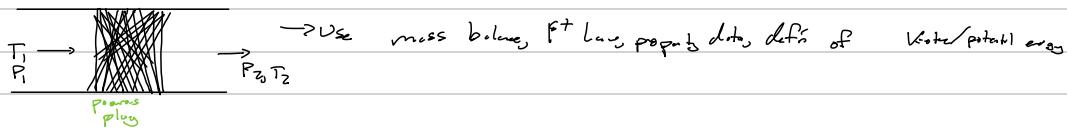
accumulation of moles

- Total mass/mole accumulation:

$$\Delta n = \dot{\nu}_{in} t - \dot{\nu}_{out} t = \int_{t_0}^{t_f} d\dot{m}$$

Example 6: Throttling Process

- Simple obstruction to reduce pressure in a pipe (constant-insulated)



Steady state: $\frac{d}{dt}(u + E_k + E_p) = 0; \frac{du}{dt} = 0 \quad \dot{m}_{in} = \dot{m}_{out} = \dot{m}$

$\dot{m}_s = 0$ (no moving parts)

$\dot{Q} = 0$ (well-insulated)

$e_{v,m} \approx 0$ (smaller than c_s) ← good approximation if velocity is much lower than the speed of sound

$e_{p,m} = 0$ (no height difference)

does change but the change is negligible with respect to other quantities

→ Simplified F+ Law

$O = \dot{m}_{in} h_{m,in} - \dot{m}_{out} h_{m,out}$

so

$$\boxed{O = h_{m,in} - h_{m,out}}$$

$$\boxed{O = \hat{h}_{in} - \hat{h}_{out}}$$

Mole Balance ($\dot{m}_{in} = \dot{m}_{out}$)

mole basis } independent of T_2
mass basis }

a) Let's assume fluid is water:

$T_1 = 350^\circ\text{C}$

$P_1 = 10 \text{ MPa}$

→ $T_2 ?$

$P_2 = 1 \text{ bar}$

Find T_2 !

$\hat{h}_1 = \hat{h}(350^\circ\text{C}, 10 \text{ MPa}) = 2923.4 \frac{\text{kJ}}{\text{kg}}$

1st law $\hat{h}_2 = \hat{h}_1$ since $\Delta h = 0$

Find T when $\hat{h}_2 = 2923.4 \frac{\text{kJ}}{\text{kg}}$ at $P_2 = 1 \text{ bar} = 0.1 \text{ MPa}$

→ At 1 bar, $\hat{h}(200^\circ\text{C}) = 2875.3 \quad \hat{h}(250^\circ\text{C}) = 2974.3$ } superheated

$$\left(\frac{2974.3 - 2875.3}{250 - 200} \right) (T_2 - 200) + 2875.3 = 2923.4$$

$$\rightarrow \boxed{T_2 = 224.293^\circ\text{C}}$$

b) What will happen if fluid is ideal gas?

1) $T_2 < T_1$

3) $T_2 = T_1$

2) $T_2 > T_1$

4) real more $\Rightarrow T_2$

Why?

→ Still: $h_{m,2} - h_{m,1} = 0$ (same first law)

$\Delta h_m = 0$

$\Delta h_m = \int_{T_1}^{T_2} dh_m = 0$ (choose prop. is constant of diff. m.)

→ Ideal G.s.: $h_m = h_m(T)$ only

$dh_m = C_{pm} dT$ for ideal g.s.

$\Delta h_m = \int_{T_1}^{T_2} C_{pm} dT = 0$

$\rightarrow C_{pm}(T_2 - T_1) = 0 \Rightarrow T_2 = T_1 = 350^\circ\text{C}$ also true if $C_{pm} = C_{pm}(T)$ [i.e., not constant]

Note: Compare H_2O + ideal gas case of throttle

- ideal gas: $h_m = h_m(T)$ only

$$dh_m = C_p dT$$

- water (real fluid): $\hat{h}_m \neq h_m(T)$ only

$$\text{So } \hat{h}_m = \hat{h}_m + b + T_2 - T_1$$

Q: What is the significance of enthalpy \hat{h}_m , the first law for open systems?

1) A more fundamental molecular quantity for flow systems

2) Sum of internal energy + flow work between system & surroundings

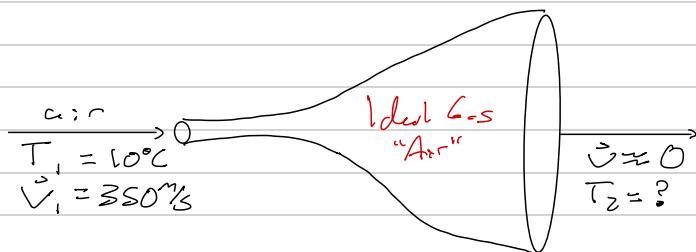
3) Flows in open systems have enthalpy \hat{h}_m , but not internal energy. Of course they have internal energy!

4) Amount of heat transferred at constant pressure

5) All of the above will do! closed systems

Ex: Nozzle or Diffuser

→ These relates to accelerate (or slow) flow streams



Process occurs @ constant pressure, $P_2 = P_1$

• Open system

• Steady state? yes!

$$\rightarrow \text{MB: } \frac{dm}{dt} = 0 = m_{in} - m_{out} \rightarrow m_{in} = m_{out}$$

• 1st Law, accumulations = 0:

$$\frac{d}{dt}(U + E_k + E_p) = 0$$

• $\dot{W}_s = 0$ no moving parts, assume adiabatic $\dot{Q} = 0$

$$\cdot e_{p,m,in} \approx e_{p,m,out} \approx 0$$

$$\cdot e_{k,m,out} = \frac{1}{2} m v_{out}^2 = \frac{1}{2} m (0)^2 = 0, e_{k,m,in} \approx 0$$

$$\cdot \text{Simpl. form 1st Law: } \hat{h}_2 = \hat{h}_1 + \hat{e}_{k,v_1} \quad \begin{matrix} \text{Solving on a mass basis} \\ \text{basis is bc of \\ kinetic energy} \end{matrix}$$

$$\rightarrow \hat{E}_{k,v_1} = \frac{1}{2} m |\vec{v}_1|^2$$

$$\hat{e}_{k,v_1} = \frac{1}{2} |\vec{v}_1|^2 = \frac{1}{2} (350 \frac{\text{m}}{\text{s}})^2 \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 61.25 \frac{\text{kJ}}{\text{kg}}$$

$$1^{\text{st}} \text{ Law} \rightarrow \hat{h}_2 - \hat{h}_1 = \hat{e}_{k,v_1}$$

$$\Delta \hat{h} = \int_{in}^{out} d\hat{h}_m = \int_{in}^{out} \hat{C}_p dT = \int_{T_1}^{T_2} \hat{C}_p dT$$

ideal g.s.

"Air": assuming ideal gas

$$\rightarrow \text{From Korets } K_{20} \hat{C}_{p,m} \approx 3.355 \text{ kJ/kgK}$$

$$\text{constant } C_p \quad \frac{K}{2 \text{ kg}} \hat{C}_p = \frac{C_p}{M W_{air}} \leftarrow (-28 \times 10^{-3} \text{ kg/mol})$$

$$\Delta \hat{h} = \int_{T_1}^{T_2} \hat{C}_p dT \approx \hat{C}_p (T_2 - T_1) = \hat{e}_{k,v_1} \rightarrow T_2 = \frac{\hat{e}_{k,v_1}}{\hat{C}_p} + T_1 \quad \text{Solve: } T_2 = 73^\circ\text{C}$$

* Note: could be more accurate w/ T-dependent $\hat{C}_p(T)$

: (macroscopic) kinetic energy "contributes" to T (macroscopic)