

# Chemistry 163B Winter 2020

## notes for lecture 5 Math and Enthalpy

Chemistry 163B  
Lecture 5 Winter 2020  
Mathematics for Thermodynamics  
Enthalpy  
Challenged Penmanship Notes

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Lecture 5: GOALS

- Some new math 'tricks'
- for ideal gas  $\Delta U = n \bar{C}_V \Delta T$  along any path (even if V changes along path)
- Derive  $C_p = C_v + nR$  for ideal gas
- New state function enthalpy, H,  $\Delta H_p = q_p$
- for ideal gas  $\Delta H = n \bar{C}_p \Delta T$  along any path (even if P changes along path)
- Use the mathematics of differentials to derive relationships among thermodynamic variables

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total differential [\(math handout item #3; E&R ch. 3\)](#)

infinitesimal change in value of state function (well behaved function)

$f(x, y)$  a well behaved function

total change in f  $\rightarrow df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$

change in f per unit change in x (along x direction)

amount of change in x

+

change in f per unit change in y (along y direction)

amount of change in y

3

differential of product (product rule)

$$d(xy) = ydx + xdy$$

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example of implication of total differentials

First Law

$$dU_{sys} = \delta q_{sys} + \delta w_{sys} + dn_{sys} \quad (n = \text{number of moles; } dn=0 \text{ for closed system})$$

U is state function  $\Rightarrow dU_{sys}$  is exact differential

for  $dn = 0$  (closed system)

$$dU(T, P) \stackrel{\text{math}}{=} \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP \stackrel{\text{first law}}{=} \delta q_{sys} + \delta w_{sys}$$

OR

$$dU(T, V) \stackrel{\text{math}}{=} \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \stackrel{\text{first law}}{=} \delta q_{sys} + \delta w_{sys}$$

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"divide through by ???" math handout item #6

$$dU(T, P) = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

how to get  $\left(\frac{\partial U}{\partial V}\right)_{X=\text{some other variable}}$  ???

"divide through by dV holding X (something else) constant"

$$\left(\frac{\partial U}{\partial V}\right)_X = \left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_X + \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_X$$

later special simplification if X=P or X=T

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**two relationships for ideal gasses: we looked ahead (lect 4 slide #5)**

- for any substance  
 $dU_v = dq_v = n\bar{C}_v dT$  and  $\Delta U_v = \int n\bar{C}_v dT$  for a constant volume process
- but for an ideal gas  
 $dU = n\bar{C}_v dT$  and  $\Delta U = n\bar{C}_v \Delta T$  for ANY path (not only constant V process)  
[other parts of path, changes of P and V with constant T, give zero contribution to  $\Delta U$ ]

- for ideal gas  
 $\bar{C}_p = \bar{C}_v + R$
- monatomic ideal gas  
 $\bar{C}_v = \frac{3}{2}R$     $\bar{C}_p = \frac{5}{2}R$   
[simple proof coming soon]

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**ideal gas  $\Delta U_{ideal\ gas} = n\bar{C}_v \Delta T$  for ANY path (not only constant V process)**

$dU_v = dq_v = n\bar{C}_v dT$  and  $\Delta U_v = \int n\bar{C}_v dT$  for a constant volume process  
 $dU_{ideal\ gas} = n\bar{C}_v dT$  and  $\Delta U_{ideal\ gas} = n\bar{C}_v \Delta T$  for ANY path (not only constant V process)

(general,  $w_{other} = 0, dn=0$ )

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

$dU = dq - PdV$  first law

$$dU_v = \left(\frac{\partial U}{\partial T}\right)_V dT = dq_v = n\bar{C}_v dT$$

$$\left(\frac{\partial U}{\partial V}\right)_T = n\bar{C}_v$$

$$dU = n\bar{C}_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\Delta U = n \int_{T_i}^{T_f} \bar{C}_v(T) dT + \int_{V_i}^{V_f} \left(\frac{\partial U}{\partial V}\right)_T dV$$

ideal gas

$$dU(T,V) = n\bar{C}_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

but  $\left(\frac{\partial U}{\partial V}\right)_T = 0$

monatomic:  $E = \frac{3}{2}nRT$  doesn't depend on V (kinetic energy only T)

$$dU = n\bar{C}_v dT$$

$$\Delta U = n\bar{C}_v \Delta T$$

even if V not constant (i.e. any path)

for  $\Delta U_{ideal\ gas}$  along general path where both T (const V) and V (const T) vary  
 $\Delta U = n\bar{C}_v \Delta T$     $\Delta U = n\bar{C}_v \Delta T$  no effect on U

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$n\bar{C}_p = \left(\frac{dq}{dT}\right)_p$     $C_p$  vs  $C_v$  (E&R 4th, p.76)    $n\bar{C}_v = \left(\frac{dq}{dT}\right)_v$

**In general**

for only P-V work and closed system ( $\delta w_{other} = 0, dn=0$ )  
 $dU = dq - P_{ext}dV$  for infinitesimal change  $P_{ext} = P_{int} = P$   
 $dq = dU + PdV$

divide by dT, V const    $n\bar{C}_v = \left(\frac{dq}{dT}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v + P \left(\frac{\partial V}{\partial T}\right)_v = n\bar{C}_v$

divide by dT, P const    $n\bar{C}_p = \left(\frac{dq}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + P \left(\frac{\partial V}{\partial T}\right)_p$

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

divide by dT, P const    $\left(\frac{\partial U}{\partial T}\right)_p = n\bar{C}_v \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$

now to get  $\left(\frac{\partial U}{\partial T}\right)_p$  in terms of T,V

**finally !!!**    $n\bar{C}_p = n\bar{C}_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + P \left(\frac{\partial V}{\partial T}\right)_p$

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**let's interpret  $C_p$  vs  $C_v$  (very general relationship) ~E&R 3.37**

recapitulating    $n\bar{C}_p = n\bar{C}_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + P \left(\frac{\partial V}{\partial T}\right)_p$

$n\bar{C}_p = n\bar{C}_v + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_p$

energy to raise T 1° const P (vol changes)

energy to raise T 1° const V

potential energy as molecules 'separate' per unit volume change

restore energy lost as P-V work per unit volume change

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**$C_p$  vs  $C_v$  for ideal gas**

$n\bar{C}_p = n\bar{C}_v + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_p$

for ideal gas  
 $V = \frac{nRT}{P}$   
 Energy, U is function of ONLY T, i.e. U=U(T)

so:    $\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{P}$

$\left(\frac{\partial U}{\partial V}\right)_T = 0$

$n\bar{C}_p = n\bar{C}_v + [0 + P] \frac{nR}{P}$

$n\bar{C}_p = n\bar{C}_v + nR$

**$\bar{C}_p = \bar{C}_v + R$  for ideal gas**

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**experimental  $C_v$  and  $C_p$  for selected gasses: how 'good' is  $C_p = C_v + nR$  ?**

Nature of gas	Gas	$C_v$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_p - C_v$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\gamma$
Monatomic	He	12.5	20.8	8.30	1.66
Monatomic	Ne	12.7	20.8	8.12	1.64
Monatomic	Ar	12.5	20.8	8.30	1.67
Diatomic	H <sub>2</sub>	20.4	28.8	8.45	1.41
Diatomic	O <sub>2</sub>	21.0	29.3	8.32	1.40
Diatomic	N <sub>2</sub>	20.8	29.1	8.32	1.40
Triatomic	H <sub>2</sub> O	27.0	35.4	8.35	1.31
Polyatomic	CH <sub>4</sub>	27.1	35.4	8.36	1.31

**R=8.31 J mol<sup>-1</sup> K<sup>-1</sup>**

**ideal gas**  
 $\bar{C}_p - \bar{C}_v = R$   
**monatomic  $\bar{C}_v = \frac{3}{2}R$**   
**diatomic  $\bar{C}_v = \frac{5}{2}R$**

$J\ mol^{-1}\ K^{-1}$   
 $\frac{3}{2}R = 12.47$   
 $\frac{5}{2}R = 20.78$   
 $\frac{7}{2}R = 29.10$

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## notes for lecture 5 Math and Enthalpy

### 1<sup>st</sup> Law recapitulation

$U \equiv$  internal energy  
 $dU_{\text{sys}} = \delta q_{\text{sys}} + \delta w_{\text{sys}} + dn_{\text{sys}}$  (n=number of moles; dn=0 for closed system)  
 $dU_{\text{sys}} = -dU_{\text{surr}}$  (energy conserved)  
 $dU$  is exact differential  
 $U$  is a state function *completely general*

for only P-V work and closed system (dn=0)

$$dU = \delta q - P_{\text{ext}} dV$$

- Constant volume process  $dU_V = \delta q_V$      $\Delta U_V = q_V$
- Adiabatic process             $dU = \delta w$      $\Delta U = w$

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### enthalpy: $q$ for process at constant Pressure

$$H \equiv U + P_{\text{int}} V \quad (\text{definition of enthalpy, } H)$$

since  $U$  is state function; and since  $P, V$  are state variables,  $H$  is also a

**STATE FUNCTION** *completely general*

why a new state function you might ask??

$$dU_V = \delta q_V \quad ; \quad \Delta U_V = q_V \quad \text{heat at constant volume}$$

but most reactions and many physical processes are carried out at constant  $P$

desire state function for  $q_P$ , heat at constant pressure

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### enthalpy: $H$ , a state function for heat transfer at constant pressure

$$H \equiv U + P_{\text{int}} V$$

$$dH = dU + PdV + VdP \quad (P_{\text{int}} = P_{\text{ext}} \text{ for infinitesimal change } dP)$$

$$dH = \delta q - PdV + \delta w_{\text{other}} + PdV + VdP$$

$$dH = \delta q + VdP + \delta w_{\text{other}}$$

and at  $P = \text{constant}$  and  $\delta w_{\text{other}} = 0$

$$dH_P = \delta q_P$$

$$\Delta H_P = q_P \quad \text{as advertised !!}$$

$$\Delta H_P = q_P \quad \text{at const } P \text{ and no } w_{\text{other}}$$

$$\Delta H_P > 0 \quad \text{endothermic (heat gained by system)}$$

$$\Delta H_P < 0 \quad \text{exothermic (heat lost by system)}$$

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### $\Delta H$ ideal gas

$$\Delta H_P = q_P = \int n \bar{C}_P dT \approx n \bar{C}_P \Delta T \quad (\text{general, for } w_{\text{other}} = 0, dn = 0)$$

but for ideal gas

$$H \equiv U + PV = U + nRT$$

$$dH = dU + nRdT \quad (\text{general for ideal gas})$$

$$dH = n \bar{C}_V dT + nRdT \quad (\text{general for ideal gas, even } V \text{ not const})$$

$$dH = n(\bar{C}_V + R)dT$$

$$dH = n \bar{C}_P dT \quad \text{IDEAL GAS ANYTIME, EVEN IF } P \text{ NOT CONSTANT}$$

$$\Delta H = n \bar{C}_P \Delta T \quad \text{ideal gas general (for } w_{\text{other}} = 0, dn = 0)$$

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### manipulating thermodynamic functions: fun and games

#### GOALS:

- Evaluate changes in thermodynamic functions in terms of selected variables

e.g.  $\left(\frac{\partial V}{\partial T}\right)_P$

- Transform expressions for changes in thermodynamic functions (e.g.  $\Delta U, \Delta H$ , etc) into expressions that can be evaluated in terms of  $P, V, T$  or other directly measurable quantities.



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### manipulating thermodynamic functions: fun and games

for example:  
HW#2

12. Derive the following for any closed system, with only P-V work:

$$C_V = - \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_U$$

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## notes for lecture 5 Math and Enthalpy

small 'cheat' via 'look ahead'

many of the results in E&R ch 3 use the below [yet] 'unproven' result; that we will derive later (using 2<sup>nd</sup> Law)

class should use result in HW2 #13\*

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

*E & R<sub>4th</sub> eqn. 3.15 [eqn.3.19]<sub>...</sub>*

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total differential for  $U(T,V,n)$  and  $H(T,P,n)$

$$U(T,V,n_1,n_2,\dots,n_N)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \sum_{i=1}^N \left(\frac{\partial U}{\partial n_i}\right)_{T,V,n_j \neq n_i} dn_i$$

$$H(T,P,n_1,n_2,\dots,n_N)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P,n} dT + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP + \sum_{i=1}^N \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j \neq n_i} dn_i$$

for now closed system all  $dn_i=0$

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$U(T,V)$ : some manipulations and relationships (closed system)

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_V dV \quad \text{closed system, } \overline{dw}_{\text{ext}} = 0$$

$$dU(T,V) = d\bar{q} - PdV$$

definition of  $C_V$ :  $\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{d\bar{q}}{dT}\right)_V = C_V = n\bar{C}_V$

'divide dU by dV, holding T constant':  $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{d\bar{q}}{dV}\right)_T - P$  *hmm (d\bar{q}/dV)\_T \stackrel{??}{=} T(\partial P/\partial T)\_V* see you later

but here we can also use our 'look ahead':  $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

to get  $dU(T,V) = n\bar{C}_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$  eqn 3.16, p 70 E&R<sub>4th</sub> [eqn.3.20 p.51]<sub>...</sub>

$\bar{C}_V, P, T, V$  and derivatives are all experimentally accessible

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$H(T,P)$ : some manipulations and relationships (closed system)

$(\partial H/\partial T)_P = C_P \quad (\partial H/\partial P)_T = ??$  in terms of P,V,T and derivatives

start:  $dH(T,P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$   
 and  $dH = dU + PdV + VdP$  closed system,  $\overline{dw}_{\text{ext}} = 0$

'divide dH by dP, holding T constant':  $\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$

chain rule:  $\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$

using  $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left[T\left(\frac{\partial P}{\partial T}\right)_V - P + P\right] + V$$

**almost fini !!**  $\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + V$  eqn 3.40 E&R<sub>4th</sub> [3.44]<sub>...</sub>

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so finishing up for dU and dH:

from previous slide  $\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + V$

similar to HW#1 prob 1d-e

$$V(T,P) dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$= \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$= \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$
 eqn 3.40 E&R<sub>4th</sub> [3.44]<sub>...</sub>

$$dU(T,V) = n\bar{C}_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$
 eqn 3.16, p 70 E&R<sub>4th</sub> [eqn.3.20 p.51]<sub>...</sub>

$$dH(T,P) = n\bar{C}_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

$\bar{C}_V, \bar{C}_P, P, T, V$  and derivatives are all experimentally accessible

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in section derive equation following equation

$$n\bar{C}_V = n\bar{C}_P + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \left(\frac{\partial P}{\partial T}\right)_V$$

start with

$$dU = dH - PdV - VdP$$

divide by dT with V constant  
and then boogie along as we just did!!

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# Chemistry 163B Winter 2020

## notes for lecture 5 Math and Enthalpy

### First Law: ideal gas calculations

relationships that apply to **ideal gasses** for all conditions with  $w_{\text{other}}=0$  and constant composition (some also apply **more generally**):

$\Delta U = q + w$	$w_{pV} = -\int P_{\text{ext}} dV$	$PV = nRT$
$q_V = n \int \bar{C}_V dT$ $\cong n \bar{C}_V \Delta T$	$q_P = n \int \bar{C}_P dT$ $\cong n \bar{C}_P \Delta T$	$\bar{C}_P = \bar{C}_V + R$
$H \equiv U + PV$	$\Delta U_{\text{any conditions}} = n \bar{C}_V \Delta T$	$\Delta H_{\text{any conditions}} = n \bar{C}_P \Delta T$
<b>monatomic ideal gas</b>	$\bar{C}_V = \frac{3}{2}R$	$\bar{C}_P = \frac{5}{2}R$

? only when  $C_V$  or  $C_P$  doesn't depend on T!

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### Lecture 5: GOALS

- ✓ Some new math 'tricks'
- ✓ for **ideal gas**  $\Delta U = n \bar{C}_V \Delta T$  along any path (even if V changes along path)
- ✓ Derive  $C_P = C_V + nR$  for ideal gas
- ✓ New state function enthalpy, H,  $\Delta H_P = q_P$
- ✓ for **ideal gas**  $\Delta H = n \bar{C}_P \Delta T$  along any path (even if P changes along path)
- ✓ Use the mathematics of differentials to derive relationships among thermodynamic variables

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END OF LECTURE 5

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### why is $C_V$ larger for diatomic than for monatomic gas?

**monatomic**  $\bar{C}_V = \frac{3}{2}R$   
**diatomic**  $\bar{C}_V \cong \frac{5}{2}R$   
**non-linear polyatomic**  $\bar{C}_V > 3R$

translational and rotational modes each contribute  $\frac{1}{2}R$  to  $\bar{C}_V$

**activated at high T**

[http://images.flatworldknowledge.com/news/flatworldknowledge/flatworldknowledge/18\\_013.jpg](http://images.flatworldknowledge.com/news/flatworldknowledge/flatworldknowledge/18_013.jpg)

heat energy goes into	translation	rotation	vibration active at 298K (total)
monatomic	3	0	0 (0)
diatomic	3	2	0 (1)
polyatomic	3	3	>0 (3N-6)

<https://www.slideserve.com/materials/Chapter-2-the-first-law-the-concepts>

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