

Chemistry 163B, Winter 2013  
Lectures 18-19 Introduction to Phase Diagrams

**Chemistry 163B**  
**One-Component**  
**Phase Diagram Basics**

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*qualitative factors in phase changes*

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*melting*  
 solid  $\rightleftharpoons$  liquid  
*freezing/fusion*  
*vaporization* ENDOTHERMIC  
 liquid  $\rightleftharpoons$  gas  $\rightleftharpoons$   
*condensation* EXOTHERMIC  
*sublimation*  
 solid  $\rightleftharpoons$  gas  
*deposition*

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*vapor pressure over pure liquid (notation)*

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$P^\bullet \equiv P^* \equiv P^0$   
Gene (many others)      E&R      Raff

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*gas  $\rightleftharpoons$  liquid as pressure increases (vary P, const T)*

---

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*liquid  $\rightleftharpoons$  vapor as heat added (vary T, const P)*

---

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*dG for phase change at constant T,P*

---

same T,P for each phase  
 $dG = -SdT + VdP + \sum_i \mu_i dn_i$   
 one component 'A' in phases  $\alpha$  and  $\beta$  constant T, P  
 $dG_{T,P} = \mu_A^{(\alpha)} dn_A^{(\alpha)} + \mu_A^{(\beta)} dn_A^{(\beta)}$   
 $dn_A^{(\beta)} = -dn_A^{(\alpha)}$   
 $dG_{T,P} = (\mu_A^{(\alpha)} - \mu_A^{(\beta)}) dn_A^{(\alpha)}$

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## Lectures 18-19 Introduction to Phase Diagrams

at equilibrium  $\mu^{(\alpha)} = \mu^{(\beta)}$ ;  $\mu$  is ESCAPING TENDENCY

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$$dG_{T,P} = (\mu_A^{(\alpha)} - \mu_A^{(\beta)}) dn_A^{(\alpha)}$$

at equilibrium  $dG_{T,P} = 0$   
 $\mu_A^{(\alpha)} = \mu_A^{(\beta)}$

for spontaneity  $dG_{T,P} < 0$

$$dG_{T,P} = (\mu_A^{(\alpha)} - \mu_A^{(\beta)}) dn_A^{(\alpha)} < 0$$

$\mu_A^{(\alpha)} > \mu_A^{(\beta)} \Rightarrow dn_A^{(\alpha)} < 0$  molecules lost from phase  $\alpha$

$\mu_A^{(\beta)} > \mu_A^{(\alpha)} \Rightarrow dn_A^{(\alpha)} > 0$  molecules gained by phase  $\alpha$

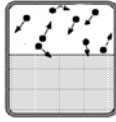
$\mu_A^{(\alpha)}$  is the **ESCAPING TENDENCY**  
for molecules in phase  $\alpha$

high  $\mu \rightarrow$  low  $\mu$   
hyper  $\rightarrow$  mellow 7


Question:

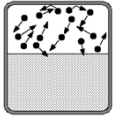
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can my pressure cooker heat water to 200C without exploding?



T=298 K  
P = 0.032 bar





T=473 K  
P = 15.5 bar

➔

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phase equilibrium one-component systems (i.e pure substances)

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$$A(\alpha) \rightleftharpoons A(\beta) \quad (T,P)$$

at equilibrium  $\Delta\mu = 0 \Rightarrow \mu_A^{(\alpha)} = \mu_A^{(\beta)}$

How can P and T covary to maintain equilibrium?

$\mu^{(\alpha)}(T_1, P_1) = \mu^{(\beta)}(T_1, P_1)$ 

T and P covary

$\downarrow d\mu^{(\alpha)}$

$\downarrow d\mu^{(\beta)}$

T and P covary

$\mu^{(\alpha)}(T_1, P_1) = \mu^{(\beta)}(T_1, P_1)$

$\xrightarrow{dT, dP}$

$\mu^{(\alpha)}(T_2, P_2) = \mu^{(\beta)}(T_2, P_2)$

before after

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conditions for remaining at phase equilibrium (one-component), covary T and P

---


$$\mu^{(\alpha)}(T_1, P_1) = \mu^{(\beta)}(T_1, P_1) \xrightarrow{dT, dP} \mu^{(\alpha)}(T_2, P_2) = \mu^{(\beta)}(T_2, P_2)$$

$$d\mu^{(\alpha)} = -\bar{S}^{(\alpha)}dT + \bar{V}^{(\alpha)}dP = -\bar{S}^{(\beta)}dT + \bar{V}^{(\beta)}dP = d\mu^{(\beta)}$$

with

$$T^{(\alpha)} = T^{(\beta)} = T \quad dT^{(\alpha)} = dT^{(\beta)} = dT$$

$$P^{(\alpha)} = P^{(\beta)} = P \quad dP^{(\alpha)} = dP^{(\beta)} = dP$$

$$-\bar{S}^{(\alpha)}dT + \bar{V}^{(\alpha)}dP = -\bar{S}^{(\beta)}dT + \bar{V}^{(\beta)}dP$$

$$(\bar{S}^{(\beta)} - \bar{S}^{(\alpha)})dT = (\bar{V}^{(\beta)} - \bar{V}^{(\alpha)})dP$$

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phase equilibrium (one-component)

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$$(\bar{S}^{(\beta)} - \bar{S}^{(\alpha)})dT = (\bar{V}^{(\beta)} - \bar{V}^{(\alpha)})dP$$

$\left(\frac{dP}{dT}\right)_{\text{phase equilibrium}} = \frac{\Delta\bar{S}_\phi}{\Delta\bar{V}_\phi}$

ϕ = phase change

eqn. 8.13 E&R

since phase change is an equilibrium (reversible) process

$$\Delta\bar{S}_\phi = \frac{\Delta\bar{H}_\phi}{T}$$

$$\left(\frac{dP}{dT}\right)_{\text{phase equilibrium}} = \frac{\Delta\bar{H}_\phi}{T\Delta\bar{V}_\phi}$$

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I. application to liquid  $\rightleftharpoons$  gas (vapor) or solid  $\rightleftharpoons$  gas

---


$$\left(\frac{dP}{dT}\right)_{\text{phase equilibrium}} = \frac{\Delta\bar{H}_\phi}{T\Delta\bar{V}_\phi}$$

vaporization – condensation    liquid  $\rightleftharpoons$  gas (vapor)

or

sublimation – deposition        solid  $\rightleftharpoons$  gas

$\bar{V}_{\text{solid}}$  and  $\bar{V}_{\text{liquid}}$  are small compared to  $\bar{V}_{\text{vapor}}$      $\Delta\bar{V}_\phi \approx \bar{V}_{\text{vapor}}$

assume ideal gas  $\Delta\bar{V}_\phi = \bar{V}_{\text{vapor}} = \frac{RT}{P}$

$$\left(\frac{dP}{dT}\right)_{\text{liquid or solid} \rightleftharpoons \text{gas}} = \frac{\Delta\bar{H}_\phi}{T \left(\frac{RT}{P}\right)} = \frac{P\Delta\bar{H}_\phi}{RT^2}$$

$$\left(\frac{d(\ln P)}{dT}\right) = \frac{\Delta\bar{H}_{\text{vap or sub}}}{RT^2}$$

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I. application to liquid  $\rightleftharpoons$  gas (vapor) or solid  $\rightleftharpoons$  gas

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$$\left(\frac{dP}{dT}\right)_{\text{or } s \rightleftharpoons g} = \frac{\Delta \bar{H}_\phi}{T \left(\frac{RT}{P}\right)} = \frac{P \Delta \bar{H}_\phi}{RT^2}$$

$$\left(\frac{d(\ln P)}{dT}\right)_{\text{equilibrium}} = \frac{\Delta \bar{H}_{\text{vap or sub}}}{RT^2}$$

Clausius-Clapeyron  
 $\approx$  eqn. 8.19 E&R

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I. application to liquid  $\rightleftharpoons$  gas (vapor) or solid  $\rightleftharpoons$  gas

---


$$\left(\frac{d(\ln P)}{dT}\right)_{\text{equilibrium}} = \frac{\Delta \bar{H}_{\text{vap or sub}}}{RT^2} \quad \text{for } s \text{ or } l \rightleftharpoons \text{gas} \quad K_f = P_{\text{gas}} \quad \left(\frac{d(\ln K_f)}{dT}\right)_{\text{equilibrium}} = \frac{\Delta \bar{H}_{\text{vap or sub}}}{RT^2}$$

$$\int_{T_1}^{T_2} d(\ln P) = \int_{T_1}^{T_2} \frac{\Delta \bar{H}_\phi}{RT^2} dT \quad (\text{assume } \Delta \bar{H} \text{ independent of } T)$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta \bar{H}_\phi}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad \text{E\&R eqn 8.20 where } \phi \text{ is vaporization similar for sublimation}$$

**application to problems:**  
to get vapor pressure given  $T^\circ_{\text{boiling}}$  and  $\Delta H_{\text{vap}}$ :

at  $T_1 = T^\circ_{\text{bp}} \quad P_1 = P_{\text{vapor}} = 1 \text{ atm}$

$$\ln\left(\frac{P_{\text{vapor}}(T)}{1 \text{ atm}}\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left[\frac{1}{T} - \frac{1}{T_{\text{bp}}}\right] = \frac{\Delta \bar{H}_{\text{vap}}}{R} \left[\frac{1}{T_{\text{bp}}} - \frac{1}{T}\right]$$

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I. application to liquid  $\rightleftharpoons$  gas (vapor) or solid  $\rightleftharpoons$  gas

---

**application to problems:** to get  $T_{\text{boiling}}$  when  $P_{\text{atm}} \neq 1 \text{ atm}$ :

$$\ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left[\frac{1}{T_{\text{bp}}} - \frac{1}{T_{\text{bp}}^\circ}\right]$$

$$T_{\text{bp}}^\circ \left(\ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right)\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left[\frac{T_{\text{bp}}^\circ}{T_{\text{bp}}} - 1\right]$$

$$T_{\text{bp}}^\circ \left(\ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right)\right) - \frac{\Delta \bar{H}_{\text{vap}}}{R} = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left[\frac{T_{\text{bp}}^\circ}{T_{\text{bp}}}\right]$$

$$\left[T_{\text{bp}}^\circ \left(\ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right)\right) - \frac{\Delta \bar{H}_{\text{vap}}}{R}\right] \left[\frac{R}{\Delta \bar{H}_{\text{vap}}}\right] = -\left[\frac{T_{\text{bp}}^\circ}{T_{\text{bp}}}\right]$$

$$\left[\frac{T_{\text{bp}}^\circ}{T_{\text{bp}}}\right] = \frac{1}{1 - \frac{RT_{\text{bp}}^\circ}{\Delta \bar{H}_{\text{vap}}} \ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right)}$$


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I. application to liquid  $\rightleftharpoons$  gas (vapor) or solid  $\rightleftharpoons$  gas

---


**application to problems:** to get  $T_{\text{boiling}}$  when  $P_{\text{atm}} \neq 1 \text{ atm}$ :

$$\left[\frac{T_{\text{bp}}}{T_{\text{bp}}^\circ}\right] = \frac{1}{1 - \frac{RT_{\text{bp}}^\circ}{\Delta \bar{H}_{\text{vap}}} \ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right)}$$




Denver: elev=1610m  $P=0.822 \text{ atm}$

$P < 1 \text{ atm} \Rightarrow \left[\frac{T_{\text{bp}}}{T_{\text{bp}}^\circ}\right] < 1 \Rightarrow T_{\text{bp}} < T_{\text{bp}}^\circ$



Death Valley: elev = -82.5 m,  $P=1.010 \text{ atm}$

$P > 1 \text{ atm} \Rightarrow \left[\frac{T_{\text{bp}}}{T_{\text{bp}}^\circ}\right] > 1 \Rightarrow T_{\text{bp}} > T_{\text{bp}}^\circ$



ouch

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II. application to solid  $\rightleftharpoons$  liquid

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$$\left(\frac{dP}{dT}\right)_{\text{phase equilibrium}} = \frac{\Delta \bar{H}_\phi}{T \Delta \bar{V}_\phi} \quad T_{\text{melting}} \text{ for phase equilibrium at } P = 1 \text{ atm} \quad \text{what is } T_{\text{melting}} \text{ at other pressures?}$$

$$\frac{dT}{T} = \frac{\Delta \bar{V}_\phi}{\Delta \bar{H}_{\text{melting}}} dP \Rightarrow \ln\left(\frac{T_{\text{melting}}}{T_{\text{melting}}^\circ}\right) = \frac{\Delta \bar{V}_\phi}{\Delta \bar{H}_{\text{melting}}} [P - 1 \text{ atm}]$$

$$\ln\left(\frac{T_{\text{melting}}}{T_{\text{melting}}^\circ}\right) = \frac{\bar{V}_{\text{liquid}} - \bar{V}_{\text{solid}}}{\Delta \bar{H}_{\text{melting}}} [P - 1 \text{ atm}]$$

will increased pressure raise or lower  $T_{\text{melting}}$  ?

$\Delta H_{\text{melting}} > 0$

(usual)  $\bar{V}_{\text{liquid}} > \bar{V}_{\text{solid}} \quad T_{\text{melting}} \text{ increases}$

(when??)  $\bar{V}_{\text{liquid}} < \bar{V}_{\text{solid}} \quad T_{\text{melting}} \text{ decreases}$

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phase rule one-component system (save proof for later)

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$f$  = degrees of freedom  
 $p$  = phases simultaneously present

2 variables :  $T, P$  (same for each phase)  
 $p-1$  restrictions:  $\mu^{(\alpha)} = \mu^{(\beta)} = \mu^{(\gamma)} = \dots$

$f$ : degrees of freedom = (variables-restrictions)  
 $f = 2 - (p-1) = 3 - p$

$f = 3 - p$

1 phase:  $T, P$  vary independently  
2 phases present:  $T$  and  $P$  covary  
3 phases present: fixed  $T$  and  $P$

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phase diagrams one component: phase vs (P,T)

BE[A]WARE: when we study multicomponent phase diagrams the axis variables may not be P,T

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phase diagrams ( $f=3-p$ )

"state" or "phase" as a function of P, T

CO<sub>2</sub>

high T  
gas  
1 phase,  $f=2$   
vary both T,P

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phase diagrams ( $f=3-p$ )

"state" or "phase" as a function of P, T

CO<sub>2</sub>

lower T  
liquid  
1 phase,  $f=2$   
vary both T,P

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phase diagrams ( $f=3-p$ )

"state" or "phase" as a function of P, T

CO<sub>2</sub>

lower T more  
solid

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phase diagrams ( $f=3-p$ )

"state" or "phase" as a function of P, T

CO<sub>2</sub>

high T  
gas  
lower T  
liquid  
lower T more  
solid

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phase diagrams ( $f=3-p$ )

"state" or "phase" as a function of P, T

CO<sub>2</sub>

low P  
gas  
raise P  
liquid  
raise P more  
solid

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two-phase equilibrium ( $p=2$ )

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$f=3-p=1$

$$\left(\frac{dP}{dT}\right)_{\text{equilib}} = \frac{\Delta\bar{H}_\phi}{T\Delta\bar{V}_\phi}$$

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phase diagrams ( $f=3-p$ )

---

liquid ↔ solid equilibrium line (melting, freezing or fusion)

$T$ 's and  $P$ 's  
for liquid ↔ solid equilibrium

2 phases,  
 $f=3-2=1$   
 $T$  and  $P$  covary

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{\Delta\bar{H}_{\text{fus}}}{T\Delta\bar{V}_{\text{fus}}}$$

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phase diagrams ( $f=3-p$ )

---

liquid ↔ gas equilibrium line (vaporization, condensation)

$T$ 's and  $P$ 's  
for liquid ↔ gas equilibrium

2 phases,  
 $f=3-2=1$   
 $T$  and  $P$  covary  
[select  $T$ , then  $P$  determined  
select  $P$ , then  $T$  determined]

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{\Delta\bar{H}_\phi}{T\Delta\bar{V}_\phi} \approx \frac{\Delta\bar{H}_{\text{vap}}}{RT^2}$$

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phase diagrams

---

solid ↔ gas equilibrium line (sublimation, deposition)

2 phases,  
 $f=3-2=1$   
 $T$  and  $P$  covary

$T$ 's and  $P$ 's  
for solid ↔ gas equilibrium

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{\Delta\bar{H}_\phi}{T\Delta\bar{V}_\phi} \approx \frac{\Delta\bar{H}_{\text{sub}}}{RT^2}$$

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critical point and triple point

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- Triple point: for a pure substance, there is only one point (value of  $T$  and  $P$ ) where all three phases (solid, liquid, and gas) can simultaneously exist in equilibrium →
- Critical point: point (value of  $T$  and  $P$ ) above which liquid and gas become one phase (fluid or supercritical fluid) →

movie: benzene critical point [A](#) [B](#)

originally from: [jchemed.chem.wisc.edu/jcesoff/cca/samples/cca2benzene.html](http://jchemed.chem.wisc.edu/jcesoff/cca/samples/cca2benzene.html)

[http://www.youtube.com/watch?v=79H2\\_QVBMGA](http://www.youtube.com/watch?v=79H2_QVBMGA)

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why does ice float ?

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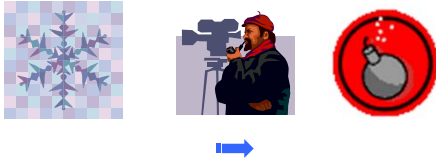
- $H_2O$  is polar and can form hydrogen bonds (mache intermolecular forces)
- High surface tension and capillarity
- Hydrogen bonds form very open structure in solid  $H_2O$  (ice) giving ice a lower density than  $H_2O$  liquid. ICE FLOATS!!

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## Lectures 18-19 Introduction to Phase Diagrams

**ice bomb !!!!**



<http://www.ice.dvvhed.org/UCESoftCCA/journals/papers/ica2orbomb.html>

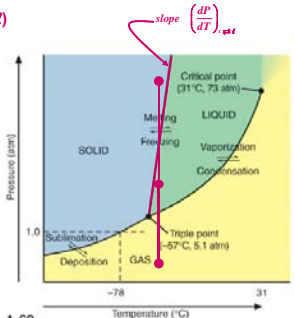
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**remember for CO<sub>2</sub> : P increases gas → liquid → solid**

CO<sub>2</sub>(s) → CO<sub>2</sub>(l)

$$\left(\frac{dP}{dT}\right)_{\text{melt}} = \frac{\Delta\bar{H}_{\text{melt}}}{T\Delta\bar{V}_{\text{melt}}}$$

$\Delta\bar{H}_{\text{melt}} > 0;$   
 $V_g > V_l \Rightarrow \Delta\bar{V} > 0$   
 $\Rightarrow \left(\frac{dP}{dT}\right)_{\text{melt}} > 0$



low P  
gas  
  
 raise P  
liquid  
(more dense)  
  
 raise P more  
solid  
(most dense)

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**phase diagram for water**

remember for CO<sub>2</sub>: P increases gas → liquid → solid

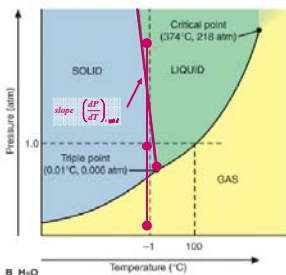
but for H<sub>2</sub>O  
as P increases:

gas  
↓  
solid  
↓  
liquid

**WHY?**  $\left(\frac{dP}{dT}\right)_{\text{melt}} < 0$   
for ice ⇒ water

$$\left(\frac{dP}{dT}\right)_{\text{melt}} = \frac{\Delta\bar{H}_{\text{melt}}}{T\Delta\bar{V}_{\text{melt}}}; \Delta\bar{H}_{\text{melt}} > 0$$

$V_g > V_l \Rightarrow \Delta\bar{V}_{\text{melt}} < 0 \Rightarrow \left(\frac{dP}{dT}\right)_{\text{melt}} < 0$




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**ice skater myth**

Does the weight of an ice skater create a pressure that melts ice to form a liquid groove for skate?

$$\ln \frac{T_{\text{melt}}}{T_{\text{frozen}}} = \frac{(\bar{V}_l - \bar{V}_s)(P - 1 \text{ atm})}{\Delta\bar{H}_{\text{fusion}}}$$

$(\bar{V}_l - \bar{V}_s) < 0 \Rightarrow \text{pressure 'melts' ice}$



E&R(3<sup>rd</sup>) Problem P8.8  
 582 bar for -4°  
 'thin blade': 78kg ≈ 172lb; -1.5°

NO, not even if they are quite 'weighty'!  
 (not enough pressure and further details of water-ice phase diagram)

e.g. Rosenberg, Robert (December 2005). "Why is ice slippery?". *Physics Today*: 50-54.

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Rosenberg, Robert (December 2005). "Why is ice slippery?". *Physics Today*: 50-54.

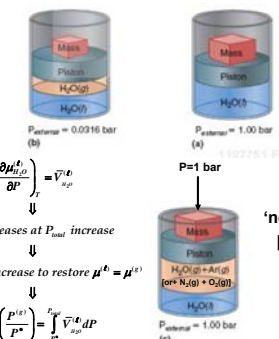


Figure 1. An ice skater exerts pressures on the order of a few hundred atmospheres on the ice surface, enough to reduce the melting temperature by only a few degrees. Premelting—the development of a liquid-like surface layer at temperatures below freezing—and frictional heating of the ice as skaters move around must account for ice's slipperiness at the wide variety of subzero temperatures found in nature. (Ice Skating, by Hy Sandham, 1885, courtesy of the Library of Congress)

The nature of the liquid-like layer is not clear from experimental measurements, so theorists have tried to clarify the situation.

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**effects of inert gas (increased total pressure) on vapor pressure**  
E&R sec. 8.7



pure H<sub>2</sub>O  
at 298K  
**P\*<sub>H2O</sub> = 0.0316 bar**

$\left(\frac{\partial \mu_{\text{H}_2\text{O}}^{\text{liq}}}{\partial P}\right)_T = \bar{V}_{\text{H}_2\text{O}}^{\text{liq}}$   
 $\mu_{\text{H}_2\text{O}}^{\text{liq}}$  increases at P<sub>total</sub> increase  
 $P_{\text{H}_2\text{O}(g)}$  must increase to restore  $\mu^{\text{liq}} = \mu^{\text{g}}$   
 $RT \ln \left(\frac{P^{\text{liq}}}{P^*}\right) = \int_{P^*}^{P^{\text{liq}}} \bar{V}_{\text{H}_2\text{O}}^{\text{g}} dP$

'normal' H<sub>2</sub>O in P<sub>total</sub>=1 bar  
 [H<sub>2</sub>O(g) + N<sub>2</sub>(g) + O<sub>2</sub>(g)]  
 at 298K  
**P<sub>H2O</sub> = 0.031622 bar**

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E&R section 8.7 (effect of inert gas on vapor pressure HW #46\*)

Temperature =  $T$

Pressure =  $P_A + P_B$

Vapor phase

Condensed phase A

$\text{H}_2\text{O}$  at 300 K  
 $P^*_{\text{H}_2\text{O}} = 0.328 \text{ atm}$

add air (inert  $\text{N}_2 + \text{O}_2$ )  
 to raise  $P_{\text{total}} = 1 \text{ atm}$

new  $P_{\text{H}_2\text{O}} = 0.32832 \text{ atm}$   
 $(P/P^*)_{\text{H}_2\text{O}} = 1.00071$

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*End of Lecture*

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