The Triple Point

A. Thermodynamics

1. *Phase Equilibria*: $X(\ell) \rightleftharpoons X(g)$ and $X(s) \rightleftharpoons X(g)$
   (vaporization and sublimation)

2. *Clapeyron Eqn*: $dP/dT = \Delta S/\Delta V$
   Since these are *equilibrium* processes at fixed T,
   $\Delta S = \Delta H/T$, where $\Delta H = \Delta H_{vap}$ or ΔH_{sub}.

3. *Clausius-Clapeyron*: When one phase is g and P is not high,

   $\Delta V \approx V_{gas} \approx nRT/P$, giving $$\frac{d\ln P}{dT} = \frac{\Delta H_m}{RT^2}$$

   or, using $d(1/T) = -\,dT/T^2$, $$\frac{d\ln P}{d(1/T)} = -\frac{\Delta H_m}{R}$$

4. *Integration*: $\ln P = const - \Delta H_m/RT$ (ΔH_m assumed const.)
   Substituting P_0 at T_0 (any reference point),

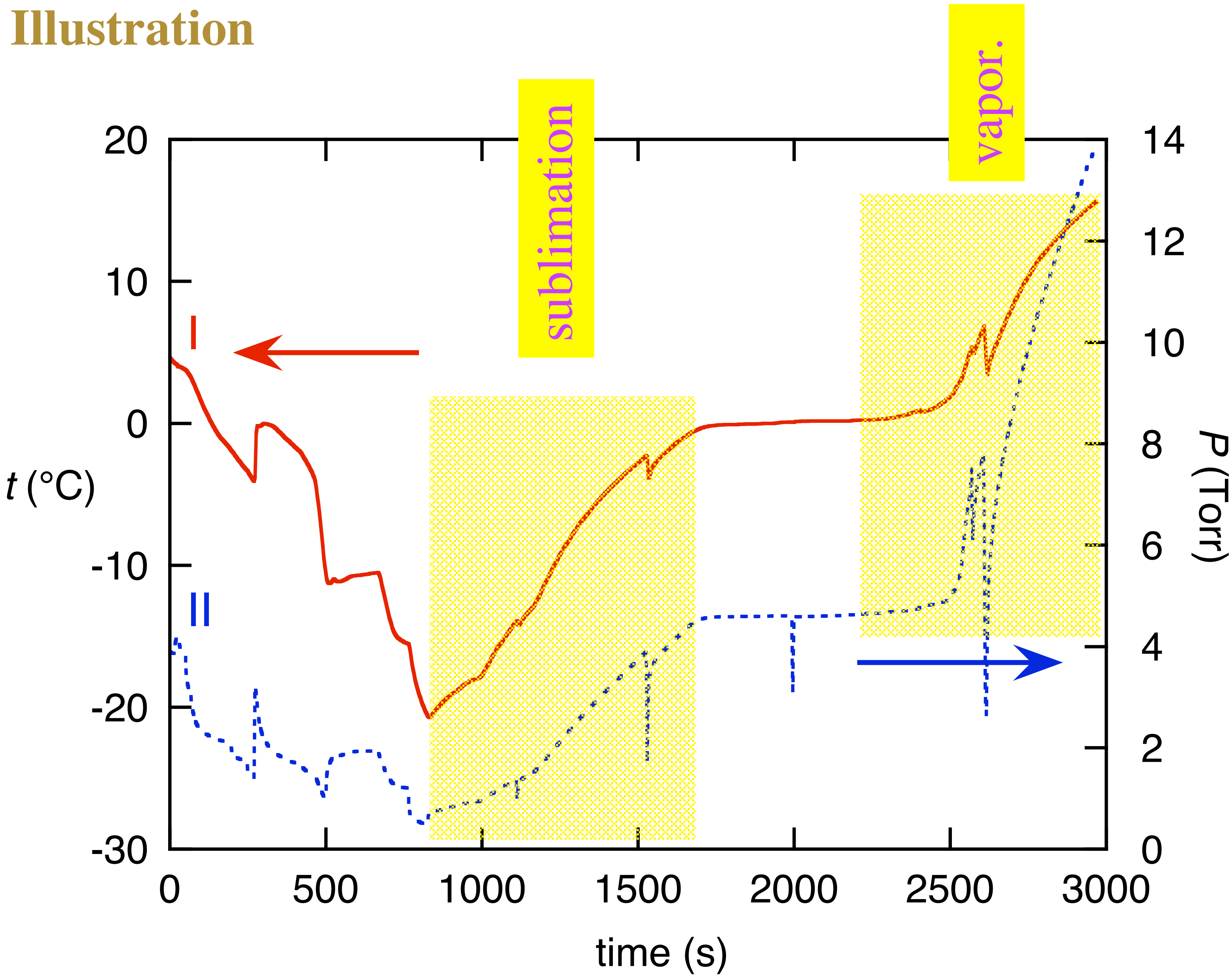
4th time!

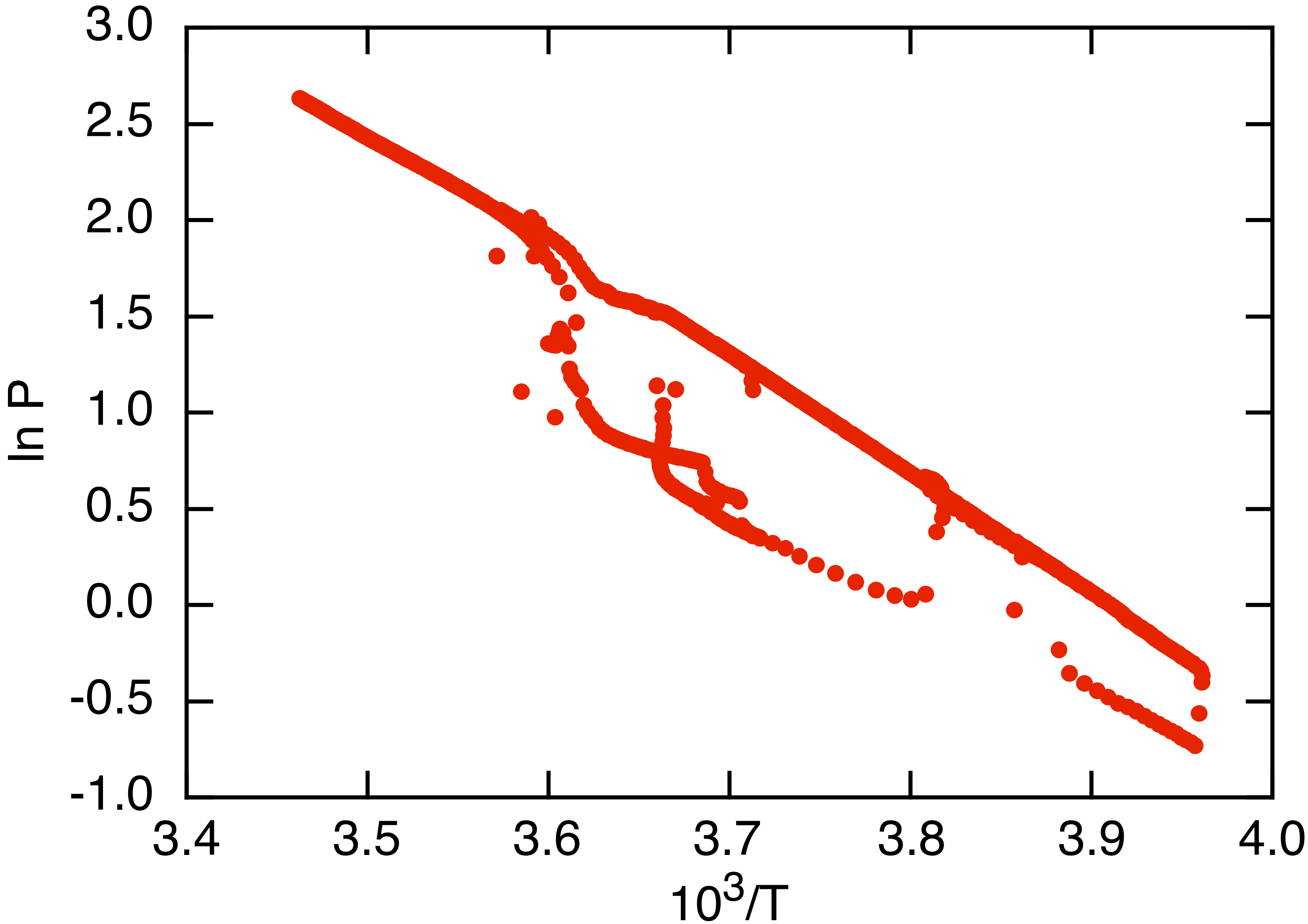
$$\ln\frac{P}{P_0} = \frac{\Delta H_m}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

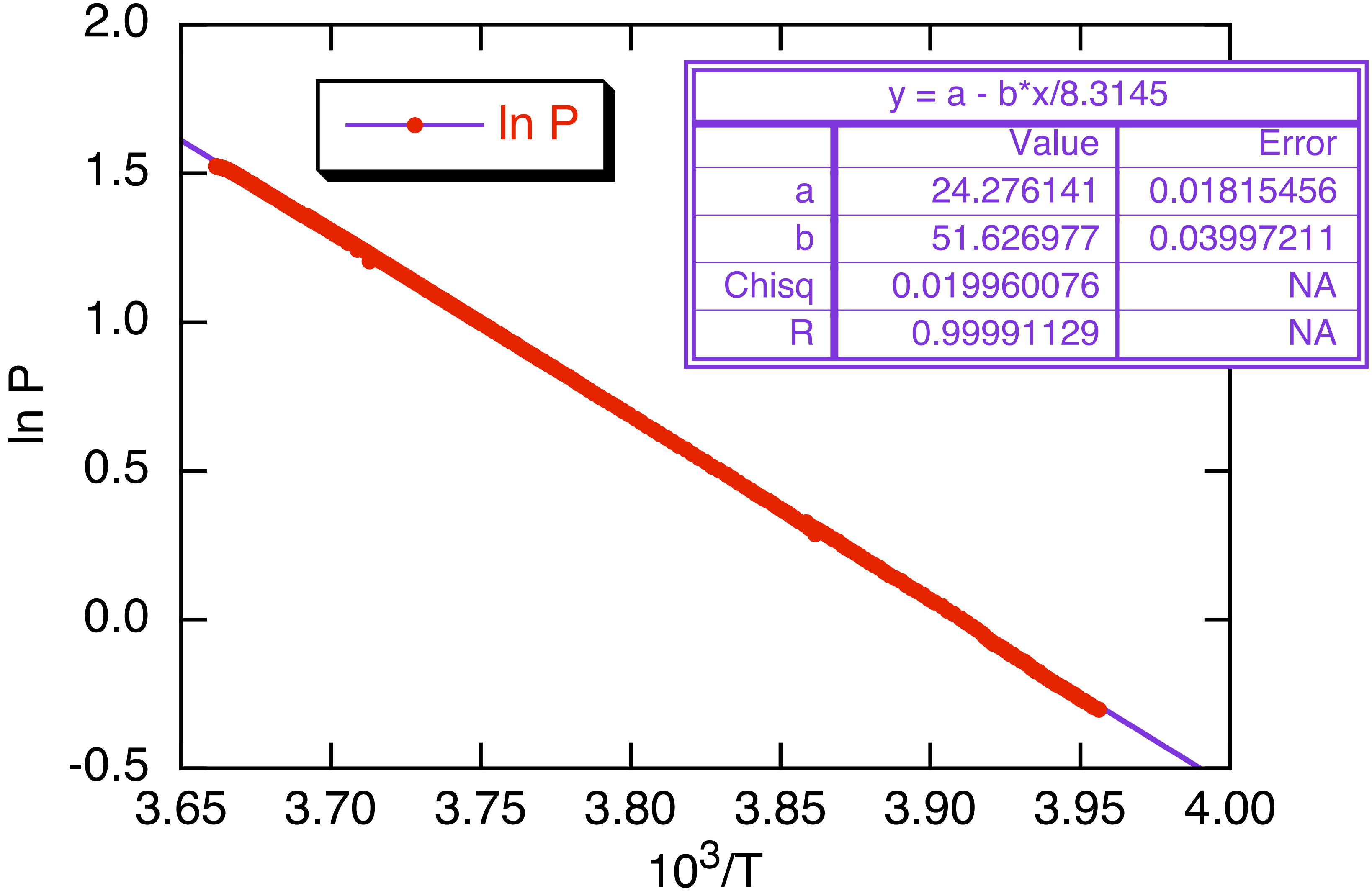
B. Experiment

1. "Freeze-dry" sample; then record P and T on warmup.
2. Edit data to remove non-equilibrium pts (if necessary).
3. Plot ln P vs. $1/T$, for sublimation *and* vaporization regions.
4. Fit to obtain ΔH_{sub} and ΔH_{vap}. and their uncertainties.
5. Calculate $\Delta H_{fus} = \Delta H_{sub} - \Delta H_{vap}$ and its uncertainty.

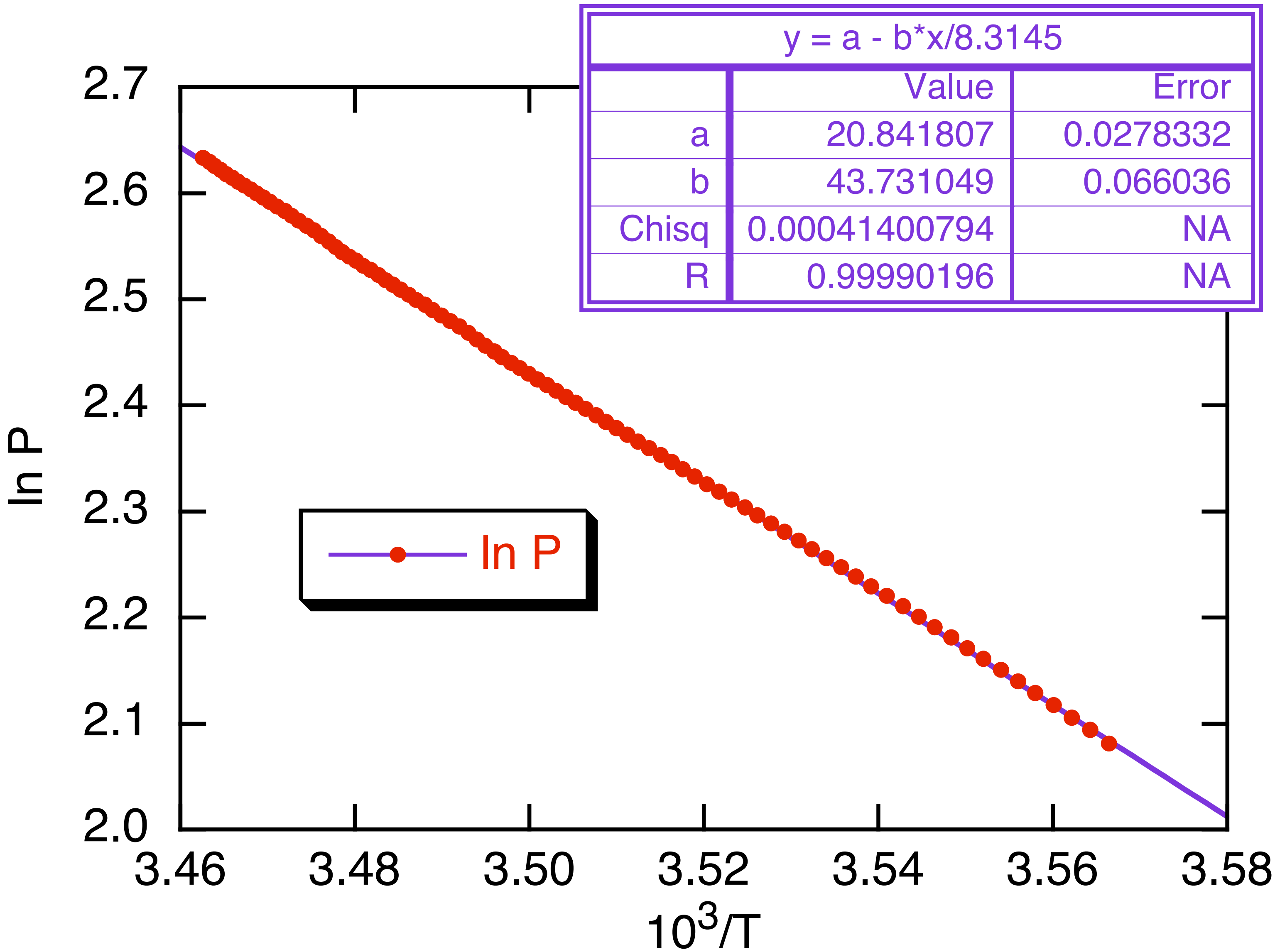
C. Illustration



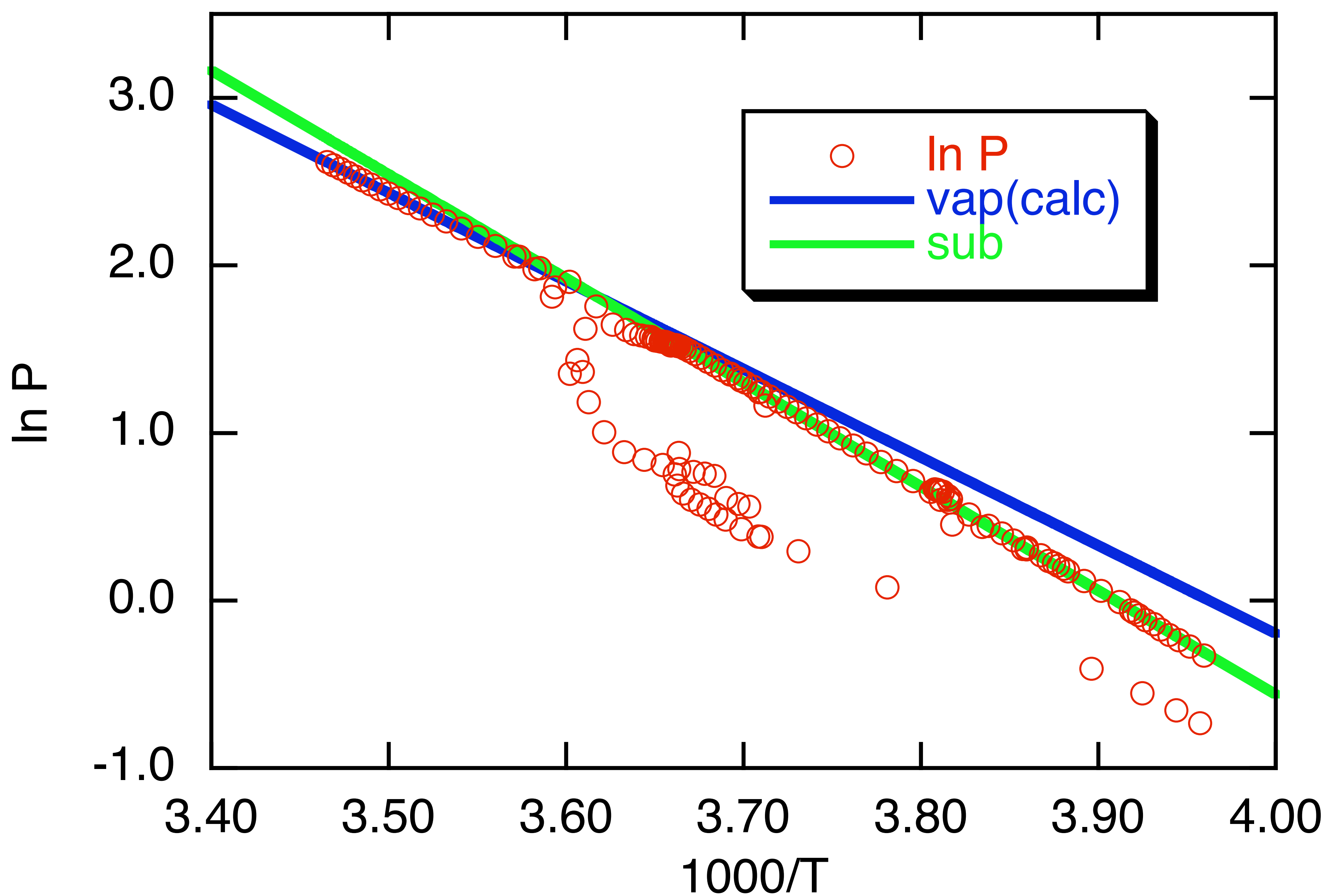

3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ln P
3.4
3.5
3.6
3.7
3.8
3.9
4.0
10^3/T



ln P
y = a - b*x/8.3145
Value
Error
a
24.276141
0.01815456
b
51.626977
0.03997211
Chisq
0.019960076
NA
R
0.99991129
NA
2.0
1.5
1.0
0.5
0.0
-0.5
3.65
3.70
3.75
3.80
3.85
3.90
3.95
4.00
ln P
10^3/T



y = a - b*x/8.3145
Value
Error
a
20.841807
0.0278332
b
43.731049
0.066036
Chisq
0.00041400794
NA
R
0.99990196
NA
ln P
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
3.46
3.48
3.50
3.52
3.54
3.56
3.58
10^3/T



ln P
vap(calc)
sub
3.0
2.0
1.0
0.0
-1.0
ln P
3.40
3.50
3.60
3.70
3.80
3.90
4.00
1000/T

Today's Practice Quiz

In KG Exer. 4 you used the random number generator to produce 10^4 random numbers in the range 0–1, then repeated for averages of 2 and 12, producing histograms and calculating statistics for all results.

- What was the appearance of each histogram?
  Roughly 1000 counts in each of 10 bins in 1st case, scatter $\sim 1000^{1/2}$
  Roughly triangular distribution for average of 2.
  Roughly normal distribution for average of 12.

2. How would the histograms differ if you had generated 10^6 total counts?
   Same shapes but smoother: Scatter is larger by factor $100^{1/2}$ but bin counts increase by factor 100, so *relative* scatter reduced by factor 10.

3. How do the means, variances, and standard deviations change for these three cases?
   Means all ~ 0.5. Variance for mean of 2 is smaller than that for single samples by factor 2; variance for mean of 12 is smaller by factor 12. □ s smaller by factors $2^{1/2}$ and $12^{1/2}$, respectively.

4. How would these results change if you generated 10^6 total counts?
   No change, just closer to theoretical expectations, thanks to the 100-fold increase in samples.

5. Jones measures *x* 16 times and obtains $\langle x \rangle = 35$ and $s_x^2 = 1$. If she now makes one more measurement, the probability that she observes a value larger than 36 or smaller than 34 is about

a. 0.50 b. 0.68 c. 0.32 d. 0.95 e. 0.05 f. >0.99 g. <0.01

6. Now Jones repeats the *entire experiment* (16 measurements). The probability that she obtains a new *average value* > 36 or < 34 is about

a. 0.50 b. 0.68 c. 0.32 d. 0.95 e. 0.05 f. >0.99 g. <0.01

7. Smith does the same experiment, using the same equipment and procedures, but makes 100 measurements. Estimate his standard deviation in the mean and compare it with Jones's value.

Smith: $s_x/N^{1/2} = {}^1/_{10}$ Jones: ${}^1/_4$